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THEORY OF INELASTIC COLLISIONS BETWEEN ATOMS

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ABSTRACT. The curves of missing interaction energy that is responsible for transitions between the two energy states are studied. Both the "general" case, in which the curves do not intersect, and the other case, where they do intersect, are treated by a new method and compared.

THEORY OF INELASTIC COLLISIONS BETWEEN ATOMS

E. C. G. Stueckelberg*

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1. Introduction

The problem of the inelastic collision of two atoms reduces, if it is permissible to consider only two electron states of each atom, always to an infinite number of systems of two simultaneous differential equations of second order with an independent variable r, which represents the distance between the center of gravity of the two systems. /370*

If the interaction energy responsible for transitions between the two electron states is small in the range of real velocities with respect to the term difference which depends on the distance, one may speak of potential energy curves of the two electron states, in accordance with Franck. The concepts of "intersecting" and "non-intersecting" then acquire in the following the meaning that curves of the missing inter-action energy are intersecting or not intersecting. The fact that transitions occur already indicates by itself that the image of potential energy curves cannot be rigorously correct.

The occurrence of an interaction always results in that the two curves repel each other in the area of overlap. The interaction between two terms can be separated into two parts: one that is independent of rotational energy and one that is dependent on the energy of rotation (quantum number J). Franck's curves are plotted entirely for J=0. If the electron terms have different symmetry properties or different quantum numbers Λ(or Ω) (= electron angular momentum quantum number around the axis connecting the nuclei), the second part disappears [1]. If this does not apply, then the second part causes the curves not to intersect for J=0 either. The curves merely approach each other. Figure 1 demonstrates the case of "intersection" and "approaching". It is thus feasible to assume in both cases that the curves intersect, depending on how the branches A_1B_1 and A_0B_0 are coordinated, because in the area of overlap the curves lose their meaning.

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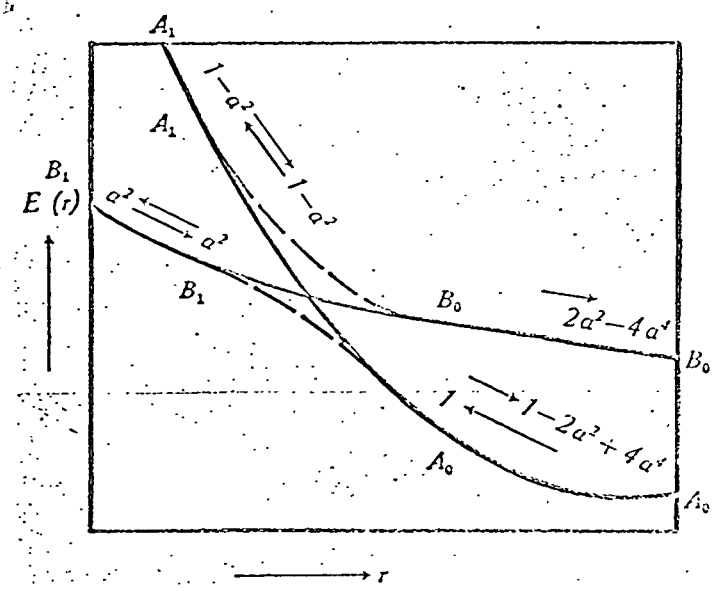

Figure 1. Intersecting energy curves for the collision of two atom systems. A_0 and A_1 possess the same characteristic electron configurations. The arrows represent the flow in the individual branches of the curves, when flow 1 arrives at branch A_0 and when each flow divides at the intersection so that part $1-a^2$ continues along the branch of the same configuration while part a^2 flows along the other branch.

If one selects the image of overlap and if the transition probablility which depends on the interaction is small with respect to 1, then Franck's concept may be accepted as valid in the first approximation even in the area of overlap and the transition probabilities determined by the interference theory. If this is, however, not true, then one may speak of "intersecting" to the extent that at the left and the right the wave functions of the electron configuration can be related to each other. The /371 "vicinity of intersection" then has properties for the asymptotic representation of the wave function similar to the points of inversion of the motion of classical mechanics. In paragraph 9 a link method, analogous to that of Wentzel, Kramers, Brillouin [2], is described, which permits the determination of transition probabilities for interaction energies of arbitrary magnitude, when the vicinity of intersection is traversed at real velocities. Let us consider a probability flow of intensity 1, which arrives "at" one of the potential energy curves (designated by A_0): it divides at the "intersection" into two flows, flow $1 - a^2$ on the A_1 curve and flow a^2 on the B_1 curve. The flows continue in the direction of arrival to their points of inversion. There they are reflected and both cross the point of inversion for a second time. Both flows are again divided so that part $(1 - a^2)$ of its intensity continues on the curve of the /372 same electron configuration, while part a^2 proceeds on the other curve. The outgoing flow $4 \cdot |\eta_1|^2$ on curve B_1 thus amounts to

$$4 \cdot |\eta_1|^2 = (1-a^2)a^2 + a^2(1-a^2) = 2a^2 \cdot (1-a^2)$$

If a^2 is designated the transition probability, it approaches the value of 1 for large interaction energies. If, however, it is designated $4|\eta_1|^2$, as will be done in the following, it attains its maximum for $a^2 = \frac{1}{2}$ with the value of $4 \cdot |\eta_1|^2 = \frac{1}{2}$ and becomes zero for $a^2 = 1$.

If the curves do not intersect and their distance can be represented approximately by a constant term difference, the "vicinity of intersection" is located at the point where the interaction energy is equal to the term difference. If this vicinity is found at imaginary velocities, the interference method is justified. If, however, the location is with real velocities, the case becomes similar to those in which curves intersect in the range of real velocities (paragraph 10).

The method is used for the determination of effective collision cross sections in collisions of the second kind. It is found that the case where no overlap occurs in the sense defined above, represents experimental results better with respect to order of magnitude and resonance character than the case of overlap. The sudden onset of ionization by rapid alkali ions, as described by Beeck, Mouzon and Nordmeyer [3] can be explained well by the intersection of potential curves [4].

The calculation of the problem has been performed heretofore from different aspects. The first, semiclassic computation by Kallmann and London [5] had the disadvantage that only the motion of electrons was treated by wave mechanics. The kinetic energy of the nuclei, which is important in the process, thus did not appear. Mores and Stueckelberg [6] applied the interference method of Born and Dirac with consideration of the finite dimensions /373 of the atoms.

The theory of the inelastic collision of slowly moving heavy mass particles must, however, as shown later by London [7] substantially differ from the theory of the inelastic collision of electrons.

If one applies formally the interference method in which the entire electrical inter-action of the two atoms is considered an interference function, a value is obtained which represents the increase per unit time in the final substance. This value, in London's notation, contains two processes:

1. the component of the "adiabatic" process, which is reconverted completely into the initial substance following the collision and thus contributes to the elastic reflection only.

2. the component of the inelastic collision.

In the collision of electrons component 1 is negligibly small, while in interatomic collisions, under certain conditions, part 1 may become substantially larger than part 2. London presented a method of separating 1 and 2. It consists of (see paragraph 7 of the present paper and paragraph 5 in London) an approach through an approximation already contained in the adiabatic process. He then applies the conventional interference method to these approximations. In the evaluation of the matrix elements obtained (London's paragraph 7), he uses neglects which in certain cases are not permissible. (See paragraph 11, this paper.)

London [7] and also the work of Morse and the author [6] assume the "general" case in which the potential energy curves upon which elastic motion takes place do not intersect. Landau [8], on the other hand, treats the case in which the curves intersect. He felt to be able to conclude that the latter case yields considerably larger effective cross sections than the "general" case.

The present paper treats both cases by a new method not based on the interference method, but which may be designated as a solution of the problem in the sense of the method of Wentzel, Kramer, Brillouin [2]. For the sake of comparison, in each case the evaluation of the corresponding matrix element by the procedures of [6, 7 and 8] is also discussed in paragraph 11. /374

2. Formulations of the Problem (Diatomic Molecule)

The treatment of the diatomic molecule is simplest in the coordinate system of Euler's angle. At least formally, these considerations may be transferred to the problem of inelastic collision.

Kronig [9] showed that in a first approximation the problem may be separated in the following manner in these coordinates:

$$\psi_{\sigma J \Lambda M T} = \frac{1}{r} v_{\sigma J \Lambda T}(r) \cdot \Theta_{J M \Lambda}(\vartheta) \cdot e^{iM\varphi} \cdot \begin{matrix}\sin \\ \cos\end{matrix} \Lambda\varphi \cdot \Phi_{\sigma\Lambda} \cdot \exp\left[-\frac{2\pi i}{h}(E_{\Lambda\sigma\infty} + T)t\right].$$

Here r is the distance of the two nuclei, ϑ the angle between the connecting axis of the nuclei (ζ axis) and a direction fixed in space (z axis), ψ and φ are the angles of the nodal line (intersection of the xy with the $\xi\eta$ plane) with the positive x and ξ axis. In the formula, ξ also indicates the entirety of the electron coordinates $\xi_i \eta_i \zeta_i$.

σ designates the quantum numbers of the electron state, Λ their rotational quantum number around the ζ axis (Λ -type doubling), J the total pulse quantum number of the system and M their projection onto the z axis. $E_{\sigma\infty}$ is the energy of the electrons (term value) and T the kinetic energy of the nuclei, both for $r = \infty$. The different functions then satisfy the equations

$$\left\{\Delta_{\xi_i\eta_i\zeta_i\ldots\varphi} + \frac{8\pi^2 m}{h^2}\left[E_{\sigma\Lambda}(r) - V(\xi_i' \eta_i \zeta_i \ldots, r)\right]\right\} \Phi(\xi_i \ldots, r) \cdot \begin{matrix}\sin \\ \cos\end{matrix} \Lambda\varphi = 0. \tag{1}$$

This is the solution with solid nuclei at a distance of r (r as the parameter).

$$\left\{\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right) - \frac{(M-\Lambda\cos\vartheta)^2}{\sin^2\vartheta} + (J(J+1)-\Lambda^2)\right\}\Theta_{JM\Lambda}(\vartheta) = 0 \tag{2}$$

$$\left\{\frac{\delta^2}{\delta r^2} + \frac{8\pi^2 M}{h^2}\left[T - E_{\sigma\Lambda}(r) - \frac{J(J+1)-\Lambda^2}{r^2}\cdot\frac{h^2}{8\pi^2 M}\right]\right\} v_{\sigma J\Lambda T}(r) = 0 \tag{3}$$ [1]

The inter-references (missing terms) are given by the operators (let $\partial/\partial r$ act on r in $\Phi(\xi_i \ldots, r)$ and $\delta/\delta r$ on r in v(r): /375

$$I + II = \frac{h^2}{8\pi^2 M}\left\{\frac{\partial}{\partial r^2} + 2\frac{\partial}{\partial r}\cdot\frac{\delta}{\delta r}\right\} + \frac{h^2}{8\pi^2 M}\cdot\frac{1}{r^2}\left\{\cos\varphi\cdot\frac{\partial}{\partial\varphi}\cdot\frac{\partial}{\partial\vartheta} + \ldots\right\}\Xi(\xi\eta\zeta), \tag{4}$$

where Ξ contains operators of the type of ξ/ζ and $\eta\partial/\partial\xi$.

(4) thus separates into two parts I and II. If the problem is again reduced to two electron states only $\sigma = 0$ and $\sigma = 1$ with Λ_0 and Λ_1, the following cases must be distinguished

Case 1: $\Lambda_0 = \Lambda_1$:

Multiplication of the left side with

$$\cdot\ \bar{\Phi}_0 \cdot e^{-iM_s\nu} \cdot \begin{matrix}\sin \\ \cos\end{matrix} \Lambda_0\varphi \cdot \Theta_{J,M,\Lambda_0}$$

1. In Equation 3 $E_{\sigma\Lambda\infty} = 0$ is used for simplicity.

and integration over the electron coordinate ξ and over ψ, φ and ϑ, (if ' indicates derivation with respect to r and if J_0^2 is written for $J_0(J_0+1) - \Lambda_0^2$ which for large values of J_0 is always permissible), yields:

$$v''_{0JT_0} + \frac{8\pi^2 M}{h^2}\left[T_0 - (E_{0\Lambda}(r) - E_{0\Lambda\infty}) - \frac{h^2}{8\pi^2 M}\cdot\frac{J_0^2}{r^2}\right]v_{0JT_0} + \int d\xi\,(\bar{\Phi}_0\,\Phi''_0\,v_{0J_0T_0} + 2\,\bar{\Phi}_0\,\Phi'_0\,v'_{0J_0T_0}) = -\int d\xi\,(\bar{\Phi}_0\,\Phi''_1\,v_{1J_0T_1} + 2\,\bar{\Phi}_0\,\Phi'_1\,v'_{1J_0T_1}) \qquad (5)$$

and a corresponding equation (if 0 and 1 are interchanged) for $v_{1J_0T_1T_0} + E_{0\Lambda\infty} = T_1 + E_{1\Lambda\infty}$. These are the conjugate equations on which London [7] bases his considerations. The coupling by the higher terms cited under II is zero or in general at least of a smaller order of magnitude since $\varphi\ \partial/\partial\varphi$ has no diagonal matrix elements in Λ.

Case II: $\Lambda_0 \mp \Lambda_1$:

This is the case treated by Landau [8]. Coupling takes place only by the second interference term II. At $J \gg 1$, the first term of II may be considered as the only essential one. (For details see Kronig [9]).

For large J, it is permissible to write: /376

$$\left|\int \Theta_{J\Lambda_0}\frac{\partial}{\partial\vartheta}\Theta_{J\Lambda_1}\,d(\cos\vartheta)\right| \sim J.$$

The $\cos\varphi\,\frac{\partial}{\partial\varphi}$ factor leads to:

1. $\Lambda_1 = \Lambda_0 \pm 1$ and
2. that coupling occurs only between $\sin \Lambda_0\varphi$ and $\cos \Lambda_1\varphi$. Further, coupling can occur only between functions with identical M values (since no $\overset{\cos}{\sin}\ \psi$ occurs) and identical J values (preservation of the total rotational momentum.)

The coupling term is

$$\frac{h^2}{8\pi^2 M}\cdot\frac{1}{r^2}\cdot\int d\xi\,\bar{\Phi}_0\,\Xi(\xi)\,\Phi_1\cdot\int \overset{\cos}{\sin}\Lambda_0\varphi\cdot\cos\varphi\cdot\overset{\sin}{\cos}\Lambda_1\varphi\cdot d\varphi \cdot\int\Theta_{J\Lambda_0}\frac{\partial}{\partial\vartheta}\Theta_{J\Lambda_1}\,d(\cos\vartheta) \simeq -\frac{h^2}{8\pi^2 M}\cdot\Lambda(r)\cdot J\cdot\frac{1}{r^2} = \underline{W^{II}_{01}(r)} \qquad (7)$$

where $\Lambda(r)$ is still a function of r. For small distances, $\Lambda(r)$ may attain the value of the quantum number Λ.

Naturally, the matrix element W^{II}_{01} must be hermetic and, since $\bar{\Phi}$ can be assumed to be real, the matrix element of the real physical entity

$$\cos\varphi\cdot\frac{h}{2\pi i}\frac{\partial}{\partial\varphi}\cdot\frac{h}{2\pi i}\frac{\partial}{\partial\vartheta} = \cos\varphi\cdot p_\varphi\cdot p_\vartheta.$$

is also real. Therefore again $W_{01}^{II} = W_{10}^{II}$ and again only two simultaneous equations:

$$v''_{0J,T_0} + \frac{8\pi^2 M}{h^2}\left[T_0 - (E_{0\Lambda_0}(r) - E_{0\Lambda_0\infty}) - \frac{h^2}{8\pi^2 M}\cdot\frac{J_0^2}{r^2}\right]v_{0J,T_0} = W_{10}^{II}(r)\cdot\frac{8\pi^2 M}{h^2}v_{1J,T_1} \qquad (5b)$$

(and correspondingly for $v_{1J_0T_1}$, if 1 and 0 are interchanged).

Considerations by Neumann and Wigner [1] yield (as shown by Landau [8]) the following:

If $\Lambda_0 = \Lambda_1$, the levels overlap only with different total spins, but then the interaction energies W_{01}^{I} are low. The interaction energies W_{01}^{II} are generally smaller than W_{01}^{I} for small values of J, however, because $\Lambda_0 \neq \Lambda_1$, an overlap of potential energy curves is possible. Landau [8] now concludes in a very clever manner that in case I, where there is no overlapping for real velocities, the transition probabilities disappear with increasing electron level distances in an exponential manner, while in case II they possess another form during overlapping. /377

In paragraphs 9 and 10 the two cases are evaluated by the new method. It will be shown that although Landau's statement concerning the exponential behavior of case I is correct, the effective cross sections of case I can be substantially greater--with good resonance--than those of case II, in spite of the overlap (paragraph 12).

3. Boundary Conditions and Effective Cross Section

Let us assume that Λ is small with respect to J, then the solutions of (2) (standardized with respect to 1) are

$$\Theta_{JM,\Lambda=0} = \sqrt{\frac{(2J+1)(J-M)!}{4\pi(J+M)!}}\cdot P_J^M(\cos\vartheta).$$

Let the wave function of nuclear motion in the 0 state represent a plane-incident and plane-reflected (elastically reflected) spherical wave. Let us assume that the v_J values, which must behave in ∞ as Bessel functions, are standardized as the latter, i.e.

$$\lim_{r=0} v_{0J} = r^{\frac{1}{2}}\left[J_{J+\frac{1}{2}}\left(p_0 r + \mu_{0J}\cdot\frac{\pi}{2}\right) + \eta_{0J} H^{(1)}_{J+\frac{1}{2}}\left(p_0 r + \mu_{0J}\cdot\frac{\pi}{2}\right)\right]; \qquad p_0^2 = \frac{8\pi^2 M}{h^2}T_0 \qquad (8a)$$

then

$$F_0 = \sum_J A_J \cdot \Theta_{J00} \cdot \frac{1}{r} \cdot v_{0J}(r) \tag{9}$$

with

$$A_J = \left[\left(J + \frac{1}{2}\right)\frac{(2\pi)^3 M}{h p_0}\right]^{\frac{1}{2}} \cdot e^{i\frac{\pi}{2}(J+\mu_J)}$$

represents in the infinite a wave of the current density 1 cm^{-2} sec^{-1}. μ_{0J} is a phase constant depending on the potential field $E_0(r) - E_{0\infty}$ and determining the elastic scatter (dispersion).

With coupling absent, v_{0J} must be a real function everywhere so that no current different from zero flows, i.e. $\eta_{0J} = 0$. /378

For v_{1J} the boundary condition in the infinite (emitted spherical wave only) is:

$$\lim_{r\to\infty} v_{1J} = \eta_{1J} \cdot r^{\frac{1}{2}} \cdot H^{(1)}_{J+\frac{1}{2}}\left(p_1 r + \mu_{1J} \cdot \frac{\pi}{2}\right); \; p_1^2 = \frac{8\pi^2 M}{h^2} \cdot T. \tag{8b}$$

The function

$$F_1 = \sum_J A_J \Theta_{J00} \frac{1}{r} v_{1J} \xrightarrow[r=\infty]{} \sum_J A_J \Theta_{J00} \cdot \eta_{1J} \cdot \frac{1}{r^{\frac{1}{2}}} H^{(1)}_{J+\frac{1}{2}}$$

then represents the outrunning spherical wave. The current F_1, flowing through the infinitely wide spherical surface is - due to the standardization of F_0 (current density 1 $cm^{-2}sec^{-1}$) - equal to the effective cross section ($d\omega$ is the differential of the spatial angle):

$$q = \frac{h}{8\pi M} \cdot \int \mathrm{imag}\,(\bar{F}_1 \nabla F_1)\, d\omega = \frac{8\pi}{p_0^2} \sum_J \left(J + \tfrac{1}{2}\right) \cdot |\eta_{1J}|^2 . \tag{10}$$

The problem thus is to solve the coupled equations (5), (5a) or (5b) with the boundary conditions (8a) and (8b) and so to determine the $|\eta_{1J}|^2$. With coupling absent, v_0 represents a standing wave, (J_{J-1}) which may be taken as the superposition of two progressing ($H^{(1)}_{J+\frac{1}{2}}$ and $H_{D+\frac{1}{2}}$). $|\eta_{1J}|^2$ is then identically zero. As soon as coupling occurs, $|\eta_{0J}|^2$ and $|\eta_{1J}|^2$ are different from 0 and progressing waves are obtained in both cases. Since $J_x = \frac{1}{2}(H^{(1)} + H^{(2)})$, the maximum value of $|\eta_{1J}| = 1/2$; $|\eta_{1J}|^2 = \frac{1}{4}$ thus means that "transition probability = 1" (see paragraph 1).

4. Formulation of the Problem by the Born-Dirac Collision Theory

As an insertion, let us base our considerations here not on the diatomic molecule but let us start (with respect to a later application) with the boundary case of separated atoms. Again, let us set the wave function equal

in zero approximation to the product of the wave functions of the electron motion and those of the motion of the nuclei. However, these functions, designated by $X(\xi)$ and $1/r \cdot u(r)$, possess entirely different meanings than the functions designated by $\Phi(\xi, r)$ and $1/r \cdot v(r)$ in paragraph 2.

$$\Psi_{\sigma J \Lambda M T} = \frac{1}{r} u_{\sigma J \Lambda M T}(r) \cdot \Theta_{J M \Lambda}(\vartheta)\, e^{i M \varphi} \cdot \begin{matrix}\sin \\ \cos\end{matrix} \Lambda \varphi \cdot \chi_{\sigma \Lambda}(\xi) \cdot \exp\left[-\frac{2\pi i}{h}(E_{\sigma \Lambda \infty} + T)\, t\right] \qquad \text{(379}$$

where X satisfies the following equation:

$$\left\{\Delta_{\xi_i \eta_i \zeta_i \ldots \varphi} + \frac{8\pi^2 m}{h^2}\left[E_{\sigma \Lambda \infty} - V(\xi_i \eta_i \zeta_i \ldots, r = \infty)\right]\right\} \chi_{\sigma \Lambda}(\xi_i \eta_i \zeta_i \ldots) \begin{matrix}\sin \\ \cos\end{matrix} \Lambda \varphi = 0 \qquad \text{(1a)}$$

The interaction energy corresponding to the first interference term I in (4) now is

$$W^I(\xi_i \eta_i \zeta_i, r) = V(\xi_i \eta_i \zeta_i, r) - V(\xi_i \eta_i \zeta_i, r = \infty). \qquad \text{(4a)}$$

We now have an ordinary function in place of the operator. Obviously, there are also operators analogous to Term II, which contain $\partial/\partial\varphi$ and $\partial/\partial\vartheta$. Naturally, the X are the eigenfunctions of the separated atoms[2].

In case I, we now have in place of (5):

$$u''_{0 J T_0} + \frac{8\pi^2 M}{h^2}(T_0 - W^I_{00}(r))\, u_{0 J T_0} = \frac{8\pi^2 M}{h^2} W^I_{01}(r)\, u_{1 J T_1} \qquad \text{(5a)}$$

and the corresponding equation for u_{1JT_1}, where

$$W^I_{ik} = \int d\xi \cdot \overline{\chi}_i(\xi) \cdot W^I(\xi) \cdot \chi_k(\xi) + \frac{h^2}{8\pi^2 M} \delta_{ik} \frac{J_i^2}{r^2}; \quad \delta_{ik} = \begin{matrix} 0\ i \neq k \\ 1\ i = k \end{matrix}.$$

The result here again is two conjugate equations, but with the advantage that coupling is static and not dynamic, as in (5). The mutual advantages of these initial equations are discussed in paragraph 7. The boundary conditions for the u are naturally the same as for the v (paragraph 3, Equations (8a) and (8b)). /380

5. Example of a Rigorous Solution[3]

Since according to the basic assumptions only two electron states can be involved, the rigorous solutions of the problems in paragraph 2(5) and in

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2. Strictly speaking, they are the eigenfunctions without interaction [7]. This definition is potentially different from that found in the text. The representation in (4a) then has a purely formal significance, similar to (1a).

3. This example is found in detail in: P.M. Morse, Rev. Mod. Phys. 4, 632(1932); the example was supplied by the present author

paragraph 4 (5a) should yield the same results. Let us make in the present section a few additional temporary assumptions, without touching on their relationship to reality. Let us begin with Eq. (5a) and assume that

$$W_{00}(r) = W_{11}(r) = \frac{\beta^2}{r^2} \cdot \frac{h^2}{8\pi^2 M}$$

also that

$$W_{01} = \underset{r}{\text{const}} = \frac{h^2}{8\pi^2 M} \cdot \alpha$$

for $r < r_0$ and equal to zero for $r > r_0$. Let us set

$$\tfrac{1}{2}(p_0^2 - p_1^2) = \psi > 0.$$
$$\tfrac{1}{2}(p_0^2 + p_1^2) = p^2$$
$$p^2 \pm \sqrt{\psi^2 + \alpha^2} = \nu_1^2$$
$$f_0 = \frac{\alpha}{p_0^2 - \nu_1^2}\,;\quad f_1 = \frac{\alpha}{p_1^2 - \nu_0^2}\,;\quad f^2 = f_0 f_1$$

then (5a) is, if $J^2 = J(J+1) - \Lambda^2 + \beta^2$

$$\left.\begin{aligned} u_0'' + \left(p_0^2 - \frac{J^2}{r^2}\right) u_0 &= \alpha u_1 \\ u_1'' + \left(p_1^2 - \frac{J^2}{r^2}\right) u_1 &= \alpha u_0 \end{aligned}\right\} \quad \alpha = 0 \text{ for } r > r_0.$$

The solutions, which are finite in the zero point, are:

$$\text{for } r < r_0 \quad u_0 = r^{\frac{1}{2}} \cdot [c_0 \cdot J_J(\nu_0 r) + c_1 \cdot f_0 \cdot J_J(\nu_1 r)]$$
$$u_1 = r^{\frac{1}{2}} \cdot [c_0 \cdot f_1 \cdot J_J(\nu_0 r) + c_1 \cdot J_J(\nu_1 r)]$$

and due to (8a) and (8b)

$$\text{for: } r > r_0 \quad u_0 = r^{\frac{1}{2}} \cdot [J_J(p_0 r) + \eta_{0J} \cdot H_J^{(1)}(p_1 r)]$$
$$u_1 = r^{\frac{1}{2}} \cdot [\eta_{1J} \cdot H_J^{(1)}(p_1 r)].$$

The equation of the two u_0 (and u_1) values in magnitude and inclination in the $r = r_0$ point yields four linear inhomogeneous equations for the determination of the four constants c_0, c_1, η_0, η_1. The solution for η_{1J} may be written in the form of a determinant of Bessel functions. The nominator is: /381

$$f_1 p_0 \cdot [H_J(p_0 r_0) \cdot J_J'(p_0 r_0) - H_J'(p_0 r_0) \cdot J_J(p_0 r_0)]$$
$$\cdot [J_J(\nu_0 r_0) \cdot \nu_1 J_J'(\nu_1 r_0) - \nu_0 J_J'(\nu_0 r_0) \cdot J_J(\nu_1 r_0)]$$
$$= \frac{2if_1}{\pi r_0^2}(\nu_0^2 - \nu_1^2) \int_0^{r_0} r\,dr \cdot J_J(\nu_0 r) \cdot J_J(\nu_1 r).$$

The denominator has the value for $\alpha^2 \ll \psi^2$ ($|f^2| \ll 1$) of:

$$-4/\pi^2 r_0^2$$

and for $\alpha^2 \gg \psi^2$ ($f^2 = -1$) the value of

$$-8/\pi^2 r_0^2$$

(as long as $\nu_1 r_0$ is real and greater than J).

As a result of the definition of $\nu_i f_i$, we obtain in both cases:

$$|\eta_{1J}| = \frac{\pi}{2} \cdot \int_0^\infty r\,dr \cdot \alpha \cdot J_J(\nu_0 r) \cdot J_J(\nu_1 r). \tag{12}$$

α here designates a function constant = α for $0 < r < r_0$ and = 0 for $r > r_0$.

For imaginary ν_1, where $\nu_1 r_0 > iJ$,

$$|\eta_{1J}|^2 = \frac{\sin x}{\sqrt{\frac{2\alpha}{p_0 p_1}} \cdot \cos\left(x + \frac{\pi}{4}\right) - i\sqrt{\frac{p_0 + p_1}{p_0 p_1}} \cdot \cos x};$$

$$x = \nu_1 r - \frac{2J-1}{4}.$$

6. Approximate Solutions (Perturbation Calculation)

The Equations (5), (5a), (5b) may be written in the form of

$$\begin{aligned} y_0'' + K_0(r)\, y_0 &= L(r)\, y_1 \\ y_1'' + K_1(r)\, y_1 &= L(r)\, y_0 \end{aligned} \tag{13}$$

where L in (5) is a linear operator. For small L (r) perturbations (weak coupling), let us set in first approximation $y_1 = 0$ and select for y_0 a solution - finite in the zero point- which, in accordance with Wentzel et al.,[2] can be standardized for positive K_0 thus

$$y_0 = y_0^{\mathrm{I}} \simeq \sqrt{\frac{2}{\pi}} \frac{1}{K_0^{\frac{1}{4}}} \cos\left(\int_{K_0=0}^{r} K_0^{\frac{1}{2}}\,dr - \frac{\pi}{4}\right)$$

(In the case of $W_{00} \sim 1/r^2$: $y_0 = r^{1/2} \cdot J_J(p_0 r)$). The homogeneous equation for y_1 again has a solution y_1^{I} finite in the zero point, and an infinite solution y_1^{II}. Let us select both so that

$$y_1^{\mathrm{I}} + y_1^{\mathrm{II}} \simeq \sqrt{\frac{2}{\pi}} \cdot \frac{1}{K_1^{\frac{1}{4}}} \cdot \exp\left[i\left(\int_{K_1=0}^{r} K_1^{\frac{1}{2}}\,dr - \frac{\pi}{4}\right)\right]$$

is normalized. Due to (13), rigorously [10]

$$y_1^{\mathrm{I}} \cdot y_1^{\mathrm{II}\prime} - y_1^{\mathrm{I}\prime} \cdot y_1^{\mathrm{II}} = \frac{2}{\pi}.$$

The solution of the inhomogeneous solution is [10]

$$y_1 = \left[c_1 + \frac{\pi}{2}\int_{\infty}^{r} d\varrho \cdot y_0^{I}(\varrho) \cdot L(\varrho) \cdot y_1^{II}(\varrho)\right] \cdot y_1^{I}(r)$$
$$+ \left[c_2 - \frac{\pi}{2}\int_{\infty}^{r} d\varrho \cdot y_0^{I}(\varrho) \cdot L(\varrho) \cdot y_1^{I}(\varrho)\right] \cdot y_1^{II}(r).$$

Boundary conditions in the infinte yield $c_2 = ic_1 = i\,\eta_{1J}$.

For r = 0, it is required that

$$\lim_{r=0}\left[\int_{\infty}^{r} d\varrho \cdot y_0^{I} \cdot L \cdot y_1^{II}\right] \cdot y_1^{I}(r) = 0,$$

which imposes a certain restriction on the perturbance interference function L(r). Since, however, the y_0^I solutions strongly disappear for r = 0 (repulsion of nuclei), the condition is generally satisfied. In addition, for r = 0, the factor y_r^{II} (r) must be zero. Because of (8b), this yields

$$-ic_2 = \eta_{1J} = +\,i\,\frac{\pi}{2}\int_{0}^{\infty} dr \cdot y_1^{I} \cdot L \cdot y_0^{I}. \tag{14}$$

Applied to the case of the preceding paragraph, (14) yields /383

$$\eta_{1J} = \frac{\pi}{2}\int_{0}^{\infty} \alpha \cdot r\,dr \cdot J_J(p_0 r) \cdot J_J(p_1 r). \tag{15}$$

The difference between (12) and (15) is that the approximating expression contains different p_i frequencies in place of ν_i in the exact expression (12). Since the integral in essence depends on the sharpness of resonance $\frac{1}{2}(p_0^2 - p_1^2) = \psi$, the error in (15) corresponds to the use of ψ in place of $\sqrt{\psi^2+\alpha^2}$. Let us prove this for a more general case.

7. Comparison of the London Approximation with the Born-Dirac Approximation

For this purpose, the method described in the preceding paragraph is applied to Equation (5) (London [7]) and Equation (5a) (Morse and Stueckelberg [6]). Let us assume that the solutions of (1a) are known. If only two states are to be considered, the two adiabatic molecular wave functions $\Phi_\sigma(r, \xi)$, which satisfy (1), may be expressed by the two functions $\chi_\sigma(\xi)$ (1a) exactly (σ = 0.1). Let us initially make the following arbitrary statement (London [7]).

$$\Phi_0 = \chi_0 \cos g + \chi_1 \sin g$$
$$\Phi_1 = -\chi_0 \sin g + \chi_1 \cos g \tag{16}$$

The χ_σ depend by definition only on ξ. (The assumption is made that the ξ_i of an electron belonging to atom I are counted from the center of gravity

of atom I. For details see London [7] in his paragraph 2 and Morse, Stueckelberg [6] in their paragraph 3). Let the as yet undetermined function depend on r only. If the χ_σ are considered normalized and orthogonal, it is readily seen that the two Φ_σ are also normal and ortogonal for all real values of g(r). This obviously is true only to the extent to which the assumption of only two electron states is valid.

The Hamilton operator of the wave equation for separate atoms is (1a) in paragraph 4:

$$H(\xi_1 \ldots \zeta_n, \varphi) = -\frac{h^2}{8\pi^2 m} \Delta_{\xi_1 \ldots \zeta_n, \varphi} + V(\xi_1 \ldots \zeta_n, r = \infty).$$

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The corresponding operator of the molecular equation (1) in paragraph 2 then is

$$H(\xi_1 \ldots \zeta_n, \varphi) + W(\xi_1 \ldots \zeta_n, r),$$

where W is defined by Equation (4a) in Paragraph 4 and by the operators mentioned there and depending on $\partial/\partial\varphi$, and $\partial/\partial\vartheta$. The Φ_σ must satisfy the following equation. (The χ_σ and thus the Φ_σ are assumed to be real):

$$\int \Phi_i (H + W)\, \Phi_k \, d\xi_1 \ldots d\zeta_n = \delta_{ik} E_i(r)$$

$$\int \chi_i H \chi_k \, d\xi_1 \ldots d\zeta_n = \delta_{ik} E_i(\infty) = \delta_{ik} E_{i\infty}.$$

The indices i and k take the place of the indices $\sigma_0 = 0$ and $\sigma_1 = 1$ in paragraphs 2 and 4. The index Λ which is meaningless here, is omitted. In addition to $E_i(r)$ and $E_{i\infty}$, the integral already defined for case (W_{01}^I) in Paragraph 4 (Equation 5a) also occurs:[4]

$$W_{ik}(r) = \int \chi_i W(\xi_1 \ldots \zeta_n, r)\, \chi_k \, d\xi_1 \ldots d\zeta_n.$$

The equation for $i \neq k$, i.e. $\delta_{ik} = 0$ yields

$$\operatorname{tang} 2g(r) = \frac{2 W_{01}(r)}{[E_{0\infty} + W_{00}(r)] - [E_{1\infty} + W_{11}(r)]}$$

and the values of levels are determined from the equations for $i = k = 0$ and $= 1$, i.e. $\delta_{ik} = 1$:

$$E_\varrho(r) = \frac{[E_{0\infty} + W_{00}] + [E_{1\infty} + W_{11}]}{2} \pm \sqrt{\frac{\{[E_{0\infty} + W_{00}] - [E_{1\infty} + W_{11}]\}^2}{4} + W_{01}^2}.$$

4. In Equation (5a), the diagonal elements W_{ii} also contain the additional term $h^2 J^2 / 8\pi^2 M r^2$, which originates in the rotation of the nuclei. In the present manner of writing these terms are not included, but are explicitly cited in (17).

The two term values (Franck's curves) therefore in this type of consideration cannot intersect with values of W_{01} other than zero, for real distances r, but can only approach each other (see [1]). As in paragraph 5, the following abbreviations facilitate writing the expression (W_{01} stands for W_{01}^{I} or W_{01}^{II}):

$$\frac{8\pi^2 M}{h^2}\cdot\frac{[E_{0\infty}+W_{00}]-[E_{1\infty}+W_{11}]}{2}=\psi(r);\ \psi(\infty)\geqslant 0;$$

$$\frac{8\pi^2 M}{h^2}W_{01}=\alpha(r);$$

$$\frac{8\pi^2 M}{h^2}T_i=p_i^2;\ p^2=\tfrac{1}{2}(p_1^2+p_0^2);$$

$$g(r)=\tfrac{1}{2}\tan g^{-1}\frac{\alpha}{\psi}$$

$$\nu_0^2=p^2-\frac{8\pi^2 M}{2h^2}[W_{00}(r)+W_{11}(r)]-\frac{J^2}{p^2}\pm\sqrt{\psi^2(r)+\alpha^2(r)};$$

$$\mu_1^2=p_0^2-\frac{8\pi^2 M}{h^2}W_{\substack{00\\11}}(r)-\frac{J^2}{r^2}=\varphi_0.$$

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As mentioned before the Φ_i are orthogonal and normal, whenever the X_i were that. And further

$$\int d\xi\,\Phi_0\,\Phi_0'=0;\quad \int d\xi\,\Phi_0\,\Phi_1'=\mp g'$$

$$\int d\xi\,\Phi_0\,\Phi_0''=-g'^2;\quad \int d\xi\,\Phi_0\,\Phi_1''=\mp g''$$

If terms with g'^2 are neglected with respect to ν_i^2, (5) becomes:

$$\begin{aligned} v_0''+\nu_0^2 v_0&=2g'v_1'+g''v_1\\ v_1''+\nu_1^2 v_1&=-2g'v_0'-g''v_0 \end{aligned}\qquad (18)$$

correspondingly, (5a) becomes

$$\begin{aligned} u_0''+\mu_0^2 u_0&=\alpha u_1\\ u_1''+\mu_1^2 u_1&=\alpha u_0 \end{aligned}\qquad (18a)$$

Equations (18) and (18a) are equivalent. The approximate definition of $|\eta_{1J}|^2$ (14), applied to (18) and (18a) may still, however, lead to different results. It follows through partial integration from (18) that:

$$\int_0^\infty v_0 v_1 g''\,dr=\int_0^\infty g\,dr\,[v_0''v_1+2v_0'v_1'+v_0v_1'']\qquad 2\int_0^\infty v_0'v_1g'\,dr=\int_0^\infty g\,dr\,[-2v_0''v_1-2v_0'v_1']$$

since g and all derivations of g for $r=\infty$, which occur, become zero and v_i and all derivations of v_i that occur, are zero for $r=0$.[5]

5. v_i and u_i signify here, corresponding to the application of paragraph 6, Eq. (14), solutions of homogeneous equations which are finite in the zero point, i.e. y_i^I.

Because of (14):

$$|\eta_{1J}| = \frac{\pi}{2}\int_0^\infty \tfrac{1}{2}\cdot \mathrm{tg}^{-1}\frac{\alpha}{\psi}\cdot(v_0 v_1'' - v_0'' v_1)\cdot dr \qquad /386$$

or because of (18) and because $\frac{1}{2}(r_0^2 - r_1^2) = \sqrt{\psi^2+\alpha^2}$:

$$|\eta_{1J}| = \frac{\pi}{2}\int_0^\infty \sqrt{\psi^2+\alpha^2}\,\mathrm{tg}^{-1}\frac{\alpha}{\psi}\cdot v_0 v_1\cdot dr. \qquad (19)$$

Correspondingly (18a) yields

$$|\eta_{1J}| = \frac{\pi}{2}\int_0^\infty \alpha\cdot u_0 u_1\, dr. \qquad (19a)$$

However, in (19): $\sqrt{\psi^2+\alpha^2}\ \mathrm{tg}^{-1}\frac{\alpha}{\psi} \simeq \alpha$ for $\alpha^2 < \psi^2$ and $\tilde{=} \frac{\pi}{2}\alpha$ for $\alpha^2 \gg \psi^2$ or $\sqrt{\psi^2+\alpha^2}\ \mathrm{tg}^{-1}\frac{\alpha}{\psi} = \delta\cdot\alpha$, where δ is a factor of the order of magnitude 1 ($1 < \delta < 1.57$), which is a sufficient approximation. The difference between (19) and (19a) is thus of the same kind as the one between the exact solution (12) and the approximate solution (15). As shown by London [7], (19a) represents the sum of adiabatic and nonadiabatic changes in state ($0 \to 1$), while (19), which is smaller due to poorer resonance, contains only the desired nonadiabatic transitions $0 \to 1$. If therefore in the range where u_{ij} is other than 0, $\alpha \ll \psi$, then the approximation method (Born-Dirac) and Equation (19a), on which the approach of and the author is based, already yield the correct answer.

Since q decomposes in a sum over J, for all J terms where

$$|\alpha_{\max}(r)| = |\alpha(r_{\min})| = \left|\alpha\left(\frac{J}{p_0}\right)\right| \ll |\psi|,$$

the method of Mores and Stueckelberg can be used.[6]

Let us therefore in the following begin with the exact adiabatic solution (Equation (5) for case I and Equation (5b) for case II), to the extent that this is possible. It will always be possible in Case II, while in Case I difficulties will be caused by the fact that the nonadiabatic interaction inducing the transitions is not merely a function but an operator. The difficulty can be avoided only by the insertion of London's approximation, which in fact transforms (see (18)) the dynamic interaction into a static interaction.

6. In Equation (17) of the present paragraph W_{01} stands for W_{01}^{I}. If the paragraph is read as a logical development of Paragraphs 2 and 4, then the W_{01} occurring in (17) earlier can mean only W_{01}^{I}. Let us establish a somewhat different convention for what follows: the parallelity between u_i with frequencies μ_i and with v_i with frequencies ν_i are generalized so that the μ_i^2 always signify a measure of the level magnitude without the perturbation responsible for the transition $\alpha = 8\pi^2 M W_{01}^{I}/h^2$ or $8\pi^2 M W_{01}^{II}/h^2$, while the r_i^2 represent term magnitudes with perturbances included. /387

8. The Link Method of Approximation Functions in the Inversion Points

In an attempt to solve the problem of conjugate equations rigorously, it is immaterial, as in paragraph 5, whether (5), (5a) or (5b) is considered, as long as the conjugation is represented by a function and not by an operator. Both pairs of equations are of the type of

$$u_0'' + \varphi_0 u_0 = \alpha u_1$$
$$u_1'' + \varphi_1 u_1 = \alpha u_0,$$

where α in case I represents the function $8\pi^2 MW_{01}^{I}/h^2$ and in case II the function $8\pi^2 MW_{01}^{II}/h^2$. In case II, calculations are thus based on the exact adiabatic approximation functions. This cannot be done in case I, because the following method of resolution of the pair of equations is not applicable to operator conjugation. Let us therefore begin with Equations (18a) in which operator conjugation is replaced by function conjugation. As shown in paragraph 7, this means that the exact adiabatic approximation functions are replaced by London's approximation functions.

In both cases, elimination yields:

$$u_0^{IV} - 2\frac{\alpha'}{\alpha}\cdot u_0^{III} + \left[\varphi_0 + \varphi_1 - \frac{\alpha''}{\alpha} - 2\frac{\alpha'^2}{\alpha^2}\right]\cdot u_0'' + \left[2\varphi_0' - 2\frac{\alpha'\varphi_0}{\alpha}\right]\cdot u_0' + \left[\varphi_0\varphi_1 - \alpha^2 - 2\alpha'\left(\frac{\varphi_0}{\alpha}\right)' - \alpha''\frac{\varphi_0}{\alpha}\right]\cdot u_0 = 0 \qquad (20)$$

and

$$u_1 = \frac{1}{\alpha}\cdot[u_0'' + \varphi_0 u_0]. \qquad (21)$$

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Let us recall that φ_i and α signify magnitudes multiplied by $1/h^2$. Let us therefore write (20a) in place of (20).

$$u_0^{IV} + D\cdot u_0^{III} + \frac{A}{h^2}\cdot[1 + h^2\cdot A_2 + \ldots]\cdot u_0'' + \frac{B}{h^2}\cdot u' + \frac{C}{h^4}\cdot[1 + h^2\cdot C_2 + \ldots]\cdot u_0 = 0, \qquad (20a)$$

where

$$A\cdot\frac{1}{h^2} = \varphi_0 + \varphi_1 = 2\varphi \qquad A_2 = \ldots$$
$$B\cdot\frac{1}{h^2} = 2\cdot\left[\varphi_0' - \frac{\varphi_0}{\alpha}\alpha'\right]$$
$$C\cdot\frac{1}{h^4} = \varphi_0\varphi_1 - \alpha^2 \qquad C_2 = \ldots$$
$$D = -2\frac{\alpha'}{\alpha} \qquad \text{ist.}$$

In accordance with the W.K.B. [2] method, here again

$$u_0 = e^{\frac{1}{h}\cdot(S_0 + hS_1 + h^2 S_2 + \ldots)}$$

and the first approximation is

$$S_0'^4 + AS_0'^2 + C = 0; \quad \frac{S_0'^2}{h^2} = i^2\nu^2 = i^2[\varphi \pm \sqrt{\psi^2 + \alpha^2}]; \quad S_1' = -\tfrac{1}{2}\frac{\nu'}{\nu} - \tfrac{1}{2}\frac{(\nu^2 - \varphi_0)' - \frac{\alpha'}{\alpha}(\nu^2 - \varphi_0)}{\nu^2 \mp \varphi}$$

etc.[7] Therefore, the same frequencies ν_0 and ν_1 occur, as in Equation (17), paragraph 5. After certain transformations, when $t = \psi/\alpha$, in second approximation the solution of (24) or (18a) thus is:

$$u_0 \simeq \left[(c_+ \cdot e^{i\int \nu_0 dr} + c_- \cdot e^{-i\int \nu_0 dr}) \cdot \exp\tfrac{1}{2}\left(-\int\frac{d\nu_0}{\nu_0} + \int\frac{dt}{\sqrt{1+t^2}}\right)\right.$$
$$\left. + (d_+ \cdot e^{i\int \nu_1 dr} + d_- \cdot e^{-i\int \nu_1 dr}) \cdot \exp\tfrac{1}{2}\left(-\int\frac{d\nu_1}{\nu_1} - \int\frac{dt}{\sqrt{1+t^2}}\right)\right] \cdot e^{-\frac{1}{2}\int\frac{t\,dt}{1+t^2}} \qquad (26)$$

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or, if $z = \alpha/\psi$:

$$u_0 \simeq \left[(c_+ \cdot e^{i\int \nu_0 dr} + c_- \cdot e^{-i\int \nu_0 dr}) \cdot \exp\tfrac{1}{2}\left(-\int\frac{d\nu_0}{\nu_0} - \int\frac{dz}{z\sqrt{1+z^2}}\right)\right.$$
$$+ (d_+ \cdot e^{i\int \nu_1 dr} + d_- \cdot e^{-i\int \nu_1 dr}) \cdot \exp\tfrac{1}{2}\left(-\int\frac{d\nu_1}{\nu_1}\right.$$
$$\left.\left. + \int\frac{dz}{z\sqrt{1+z^2}}\right)\right] \cdot e^{\frac{1}{2}\int\frac{dz}{z(1+z^2)}} \qquad (h)$$

Approximation is good everywhere except in the vicinity of the $\nu_0 = 0, \nu_1 = 0$, $\nu_0 \tilde{=} \nu_1$ points, because there the amplitudes depending on ν_i or t or z vary rapidly. During passage through or bypass of these points, abrupt changes occur in the constants c_+, c_-, d_+, d_-. For a second degree equation (points $\nu_i = 0$) the problem was executed by Kramers [2] for passage on the real axis and by Zwaan [11] for bypassing on the complex r plane. Let us use here a method similar to Zwaan's, which may be extended to the points $\nu_0 = \nu_1$. For this, one must assume that the functions φ_0, φ_1 and α are analytical in the small range under consideration. Then, u_0 must also be analytical. After circumvention of each $\nu_0 = 0$, $\nu_1 = 0$, $\nu_0 = \nu_1$ point, u_0 must return to its initial value. However, the approximate expressions do not conform. For this reason, the constants must vary steplike in certain locations. Since ν_0

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7. If the terms D and B/h^2 are included in zero approximation, four different complex fundamental frequencies are obtained, where $\nu_{0+} = -\nu_0$ is not true. This indicates for what follows that the points of inversion $\nu_{0+} = \nu_{0-}$ are in complexes. The rest of the treatment, however, remains the same.

interchanges with $-\nu_0$ in the circumvention of $\nu_0 = 0$ and $\nu_0 - \nu_1$ with $-(\nu_0 - \nu_1)$, i.e. ν_0 with ν_1 in the circumvention of $\nu_0 = \nu_1$, these steps must be proportional to the existing c_+, d_+, c_-, d_- constants (see Stokes [12]). In the circumvention of $\nu_0 = 0$, one considers

$$\nu_0^{-\frac{1}{2}} \cdot \left[c_+ \cdot e^{i\int_0^x \nu_0 dx} + c_- \cdot e^{-i\int_0^x \nu_0 dx} \right].$$

Because ν_0 is the root of an analytical function which disappears in the point $\nu_0 = 0$, $x = 0$, then, if c_+', c_-' are the constants after circumvention,

$$c_+' = c_- \cdot e^{i\frac{\pi}{2}}; \quad c_-' = c_+ \cdot e^{i\frac{\pi}{2}}. \qquad /390$$

The question of the location where the constants can step, now arises. Stokes [11, 12] showed that the approximations used, corresponding to the asymptotic representations, in the directions from the point $x = 0$, where the ratio of the two functions

$$\exp\left(\pm i\int_0^x \nu_0 d x\right)$$

assumes an extreme value, produce an error in the larger function that is greater than the absolute value of the smaller one. The constant of the smaller function thus is allowed to change steplike there. This is valid only if the discontinuity lines under consideration, without intersecting discontinuity lines coming from other points, can be followed to distances where

$$\exp\left(\pm\int_0^x \nu_0 d x\right)$$

becomes arbitrarily large or small. The equation of the discontinuity lines of c_+ is: [8]

$$\arg\left(+i\int_0^x \nu_0 d x\right) = \pi + (\text{integer} \times 2\pi)$$

If $\lambda(x)$ designates the argument of $\nu_0(x)$ and φ' the argument of dx, then (if $x = \rho \cdot e^{i\varphi}$),

$$\lambda(\rho, \varphi) + \varphi' = \pi + (\text{integer} \times 2\pi)$$

---

8. Let a be a complex number $a = a \cdot e^{i\varphi}$, then $\arg a = (\log a - \log a)/i = \varphi$. Here and in the following paragraphs, the letters φ, ψ and ϑ are used as arguments of complex numbers. Confusion with the values φ and ψ, as defined in Equation (17) paragraph 7, which represent values of levels or differences in levels, is not to be expected; the same is true for the Euler's angles in paragraphs 2 and 4.

leads to the differential equation:

$$\tan g^{-1}\left(\frac{\varrho\, d\varphi}{d\varrho}\right) + \varphi + \lambda(\varrho, \varphi) - \pi = \text{(integer x 2 } \pi) + 0.$$

It is readily seen that the extreme directions depart from the x = 0 point under the angles

$$\varphi = \frac{\pi}{3} \text{ und } \frac{5\pi}{3}$$

for steps of c_+ and under $\varphi = \pi$ for steps of c_- (see Figure 2). Let us now assume that when these directions are exceeded, c_+ varies proportionally with c_- and vice versa. (If it would be assumed that the steps are proportional to themselves and to the constants d_+ and d_-, the additional constants of proportionality would become 0). /391

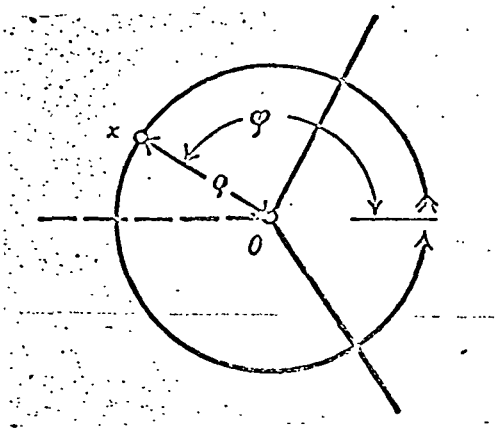

Figure 2. The x plane in the vicinity of x = 0. The discontinuity lines depart from point x = 0 under angles of $\pi/3$, π, $5\pi/3$.

We now have an initial value of c_+, c_- after exceeding $\varphi = \pi/3$:

$$c_+ + \alpha c_-;\ c_-^{*})$$

after exceeding $\varphi = \pi$

$$c_+ + \alpha c_-;\ \beta c_+ + (1 + \alpha\beta)\, c_-$$

after exceeding $\varphi = 5\pi/3$:

$$c_+(1 + \beta\gamma) + c_-(\alpha + \gamma + \alpha\beta\gamma);\ \beta c_+ + (1 + \alpha\beta)\, c_-$$

The last values must be equal to $c_- \cdot e^{i\frac{\pi}{2}}$ and $c_+ \cdot e^{i\frac{\pi}{2}}$. With the exception of the negligible factor $e^{2\pi i}$, the constants α, β, γ are thus defined by

$$\alpha = \beta = \gamma = e^{i\frac{\pi}{2}}.$$

Let us now require that on the negative real x axis, where ν_0 is imaginary, only the negative real exponent occurs ($c_+ = 0$, $c_- = c$), then the solution on the positive x axis, after exceeding $\varphi = 5\pi/3$, is:

$$\nu_0^{-\frac{1}{2}} \cdot c\left[e^{i\int_0^x \nu_0\, dx - i\frac{\pi}{2}} + e^{-i\int_0^x \nu_0\, dx + i\frac{\pi}{2}}\right]. \qquad /392$$

On the real axis, the zero location of ν_1 also occurs. It is treated in the same manner. If the zero locations of $\psi^2 + \alpha^2$, situated in the complex range,

9. The value of $\alpha = 8\pi^2 MW_{01}/h^2$ should not be confused with the symbols α, β, γ for the step constants as used here.

are neglected, u_0 would be equal to the above expression in the infinite and u_1 equal to an analogous expression. The boundary conditions of (8a) and (8b) can therefore be satisfied only for $\eta_0 = \eta_1 = 0$ (i.e. both flows = 0). The impact phenomenon must therefore be explained by the points $\nu_0 = \nu_1$, which are always in the complex range but for small perturbances near the real axis.

Because the treatment of Case II (Landau [8]) is clearer, let us consider it first in the following paragraph.

9. The Link Method of Approximation Functions in the Vicinity of Intersection (Case II)

In a small range around the intersection location $\psi = 0$, $r = r_0$, it is permissible to set α = constant and $\psi = \psi' \cdot (r - r_0)$. It is then seen that the points $\nu_0 - \nu_1 = 0$ are symmetrical and close to the real x axis. The discontinuity lines, as shown below, are located so that only one of three lines intersects with the real axis and thus connects the two points. The four others continue in pairs into the positive and negative imaginary half planes. Case II is shown in Figure 3. In the link method, this small area must be circumvented approximately in the manner indicated. The considerations

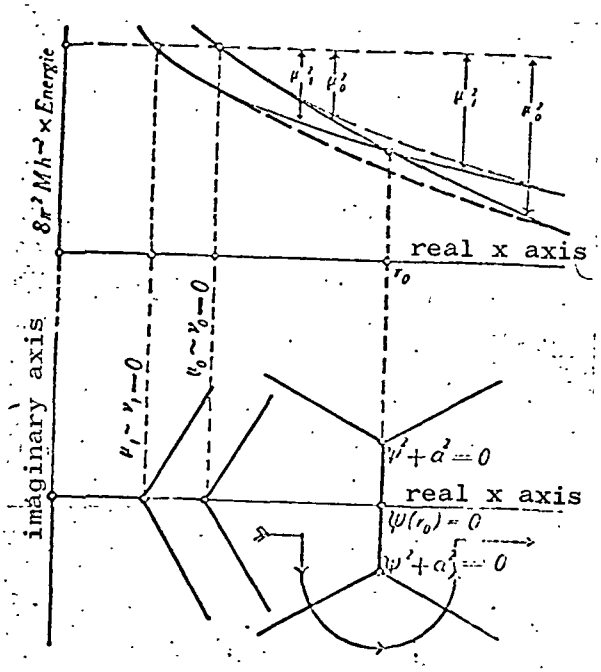

Figure 3. The upper half of the figure represents the overlap of potential energy curves μ_0^2 and μ_1^2 occurring after the conjugation has been neglected. The broken curves indicate ν_0^2 and ν_1^2. They do not intersect, but merely approach each other. Since at locations far from the intersection of the $\nu_0 \sim \mu_0$ and $\nu_1 \sim \mu_1$, the ν_i lose their identity at the intersection.
The lower half represents the corresponding complex r plane for small perturbations α. If the circumvention indicated is described, the sign of $\sqrt{\psi^2 + \alpha^2}$ changes. ν_0 which is smaller at the left side, now becomes larger at the right side than ν_1. The correlation required in the upper half is thus obtained readily. The discontinuity lines of the inversion and intersection points are indicated (solid lines).

of this paragraph are, however, valid in numerous cases where α is not small, as will be shown later (i.e. also when curves do not intersect in accordance with the procedure of Neumann and Wigner [1] described in the introduction and in Paragraph 7). The only condition is that α and ψ must be representable by an analytical function in the area required. In order to include this case from the beginning, let us assume $t = \psi/\alpha$ as the independent variable. If the area is then small, it signifies merely a change in scale, because then $t = \psi'/\alpha \cdot (r - r_0) = \text{const} \cdot (r - r_0)$. The lower limit of the integrals in the exponents of (22) can be chosen arbitrarily by separating a factor going into the constants. Let us select e.g. point B as shown in Figure 4 and separate

$$\int_B^t \nu_0\, dr = \int_B^t \frac{\nu_0 + \nu_1}{2}\, dr - \int_B^t \frac{\nu_0 - \nu_1}{2}\, dr$$

and correspondingly $\int_B^t \nu_1 dr$. /393

The first integral has no extreme directions departing from the intersection and returns to its initial value after circumvention of each of the two points.

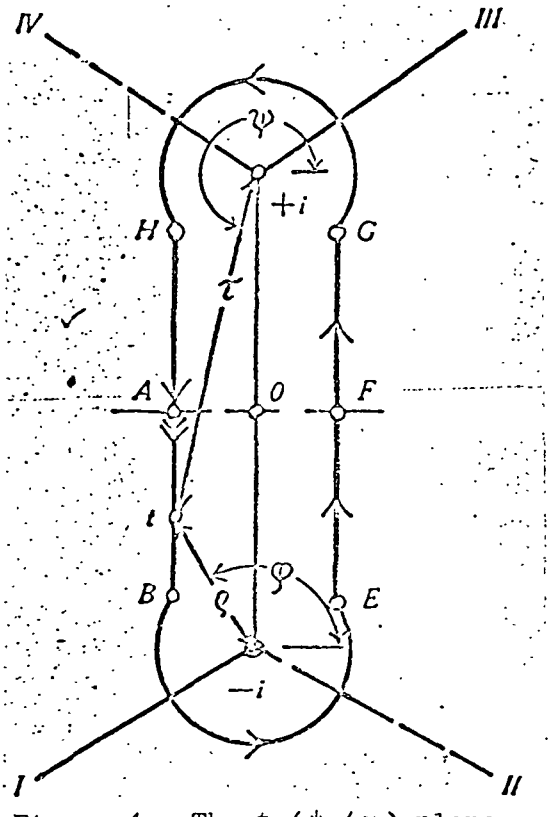

Figure 4. The $t-(\psi/\alpha)$ plane in the vicinity of $t = 0$ for constant ψ' and α. The discontinuity lines depart from the $\pm i$ points at angles which differ by $2\pi/3$ from each other.

The second, however, has extreme directions and its sign varies after circumvention of one of the points $t = \pm i$.

We now have four terms with the exponent

$$\pm i \int \frac{\nu_0 - \nu_1}{2}\, dr = \pm i \int T(t) \cdot \sqrt{1 + t^2} \cdot dt,$$

$$\text{where} \quad T(t) = \frac{\alpha}{t'(\nu_0 + \nu_1)} \qquad /394$$

The values of α, t', ν_0 and ν_1 are assumed to be functions of t. Assuming that T(t) is constant in the area needed to circumvent the points $t = \pm i$, one obtains Figure 4. The solid lines represent the curves

$$\arg\left(+i \int_{\pm i}^{t} \sqrt{1 + t^2} \cdot dt\right) = \pi + m \cdot 2\pi,$$

and the broken lines the curves

$$\arg\left(-i \int_{\pm i}^{t} \sqrt{1 + t^2}\, dt\right) = \pi + m \cdot 2\pi$$

It is stated that /395

$$\sqrt{1+t^2} = \sqrt{(t-(-i))\cdot(t-(+i))} = \varrho^{\frac{1}{2}}\cdot e^{i\frac{\varphi}{2}}\cdot\tau^{\frac{1}{2}}\cdot e^{i\frac{\psi}{2}}*)$$

with

$$\frac{\pi}{2} < \varphi < \frac{5\pi}{2}$$

and

$$\frac{3\pi}{2} < \psi < \frac{7\pi}{2}$$

(see Figure 4). The determination of the step coefficients may be achieved in a rigorous manner but is rather complicated. It is shown that the constants of $\exp(+i\int \nu_0 dx)$ change only proportionally to the constants of $\exp(+i\int \nu_1 dx)$, etc. The determination becomes much simpler if this result is anticipated. In order to simplify the expression the negligible function

$$\exp\left(i\int\frac{\nu_0+\nu_1}{2}dr\right)$$

is eliminated. Then, we have only the conjugation between the two sums in

$$\left[\begin{array}{l} \nu_0^{-\frac{1}{2}}\cdot C_+\cdot e^{\,i\int_B^t dt\cdot T\cdot\sqrt{1+t^2}+\frac{1}{2}\int_B^t\frac{dt}{\sqrt{1+t^2}}} \\ +\nu_1^{-\frac{1}{2}}\cdot D_+\cdot e^{-i\int_B^t dt\cdot T\cdot\sqrt{1+t^2}-\frac{1}{2}\int_B^t\frac{dt}{\sqrt{1+t^2}}} \end{array}\right]\cdot\exp\left(-\frac{1}{2}\int_B^t\frac{t\,dt}{1+t^2}\right)$$

where

$$C_+ = c\cdot e^{\,i\int_0^B \nu_0 dx - i\frac{\pi}{2}} \quad \text{and} \quad D_+ = d\cdot e^{\,i\int_0^B \nu_1 dy - i\frac{\pi}{2}}$$

to consider. However, the line connecting i with -i must not be used for circumvention, because there

$$\left[i\int_{t=\pm i}^{x}\frac{\nu_0-\nu_1}{2}dx\right]$$

cannot grow arbitrarily large. The path indicated in Figure 4 of A-B-E-F-G-H-A is permissible if the discontinuity lines of the points ν_0 and $\nu_1 = 0$ either /396 do not intersect the lines I, II, III and IV or do so at very large values of the exponents (at x_∞). The error of the order of magnitude then is

$$\exp\left(-\left|i\int_{t=i}^{x_\infty}(\nu_0-\nu_1)\,dx\right|\right).$$

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* See note on p. 390.

If the solution describes the path from B to E (in Figure 4), then C_+ first jumps to $C_+ + aD_+$ and then by D_+ to $bC_+ + (1 + ab)D_+$. On its way from B to G over F, the first term is also multiplied by

$$M_1 = \exp\left(i\int_B^G T \cdot dt \cdot \sqrt{1+t^2} + \int_B^G \frac{dt}{2\sqrt{1+t^2}}\right)$$

and the second term by $N_1 = M_1 - 1$ so that at C the solution is

$$\left[\nu_0^{-\frac{1}{2}} \cdot \Gamma_+ \cdot e^{i\int_G^I dt \cdot T \cdot \sqrt{1+t^2} + \frac{1}{2}\int_G^I \frac{dt}{\sqrt{1+t^2}}} + \nu^{-\frac{1}{2}} \cdot \Delta_+ \cdot c \quad -i\ldots\right]$$
$$\cdot \exp\left(-\tfrac{1}{2}\int_B^I \frac{t\,dt}{1+t^2}\right)$$
$$\Gamma_+ = (C_+ + aD_+) \cdot M_1;\quad \Delta_+ = (bC_+ + (1+ab)D_+) \cdot N_1.$$

By circumventing +i from G to H, Γ_+ changes to $\Gamma_+ + \alpha\Delta_+$ and Δ_+ to $\beta\Gamma_+ + (1 + \alpha\beta)\Delta_+^*$). On the way from G to B over A, the corresponding factors of M_2 and N_2 are added.

$$\log M_1 M_2 = \log N_1 N_2 = \frac{1}{2}\oint \frac{dt}{\sqrt{1+t^2}} + i\oint T\sqrt{1+t^2}\cdot dt = i\pi - 2\delta;$$
$$\log M_1 N_2 = \log M_2 N_1 = 0$$
$$\frac{1}{2}\oint \frac{t\,dt}{1+t^2} = i\pi.$$

($\oint$ is the line integral on the path of A-B-E-F-G-H-A). /397

The positive real value δ is determined as follows:

The integral $i\oint T \cdot \sqrt{1+t^2} \cdot dt$, is, since T analytically $= T_0 + tT_0' + \ldots$,

$$i\oint T \cdot \left(1 + \frac{1}{2}\cdot\frac{1}{t} + \ldots\right)\cdot dt = i\oint T_0 \cdot \frac{1}{2}\cdot\frac{dt}{t} = -\pi \cdot T_0 = -2\delta,$$

because $|t| > 1$ over the entire path, if desired. After the circumvention, ν_0 and ν_1, also $\nu_0 - \nu_1$ (in contrast to the points $\nu_0 = 0$) return to their initial values. The following two determination conditions are obtained:

$$-[C_+(\alpha b - e^{-2\delta}) + D_+(\alpha(1+ab) - ae^{-2\delta})] = C_+$$
$$-[C_+(\beta - b(1+\alpha\beta)e^{+2\delta})$$
$$+ D_+(\beta a - (1+ab)(1+\alpha\beta)e^{+2\delta})] = D_+.$$

This yields four equations for the determination of four constants. It is found that (with the exception of the factor $e^{2\pi i}$):

$$\alpha = \beta = a = b = c^{i\frac{\pi}{2}} \cdot \sqrt{1 - e^{-2\delta}}.$$

(In the case of a rigorous solution of the problem, a total of 4 x 4 = 16 constants were to be determined, of these the eight which conjugate ν_0 with ν_1 and vice versa, are zero.)

The constants which conjugate C and D have the same value as α, β, a, b.

If $e^{-2\delta} \ll 1$, the points are widely separated or isolated. An isolated point thus has 3 discontinuity lines and the step coefficients are $e^{i\frac{\pi}{2}}$. This is in agreement with the values found for $\nu_0 = 0$ (Figure 2). If the points coincide ($T_0 = \delta/2\pi = 0$), the step coefficients are all = 0. ($T_0 = 0$ means, however, $\alpha = 0$, i.e. no interaction). The solution left of $\psi = 0$, i.e. on the negative real t axis, is known; it is given by Equation (22), when $c_+ = c \cdot e^{i\frac{\pi}{4}}$ and $d_+ = d \cdot e^{i\frac{\pi}{4}}$. Description of the path of A-B-E-F and considering that for reasons of symmetry

$$i\int_A^F \frac{\nu_0 - \nu_1}{2}\, dr = \frac{i}{2} \oint T(r) \cdot \sqrt{1 + t^2} \cdot dt = -\delta$$

/398

the solution on the real axis right of $\psi = 0$ (see Figure 4), i.e. on the positive real t axis

$$u_0 = \frac{1}{\nu_0^{\frac{1}{2}}} \cdot \left[\frac{\psi + \sqrt{\psi^2 + \alpha^2}}{\sqrt{\psi^2 + \alpha^2}}\right]^{\frac{1}{2}} \cdot \left[(c \cdot e^{-\delta} + d \cdot \sqrt{1 - e^{-2\delta}} \cdot e^{-i\tau})\, e^{i\int_0^x \nu_0 dx - i\frac{\pi}{4}}\right.$$
$$\left. + (c \cdot e^{-\delta} + d \cdot \sqrt{1 - e^{-2\delta}} \cdot e^{+i\tau})\, e^{-i\int_0^x \nu_0 dx + i\frac{\pi}{4}}\right]$$
$$- \frac{1}{\nu_1^{\frac{1}{2}}} \left[\frac{\alpha^2}{\psi\sqrt{\psi^2 + \alpha^2} + \psi^2 + \alpha^2}\right] \cdot \left[(-c \cdot \sqrt{1 - e^{-2\delta}} \cdot e^{i\tau} + d \cdot e^{-\delta})\, e^{i\int_0^y \nu_1 dy - i\frac{\pi}{4}}\right.$$
$$\left. + (-c \cdot \sqrt{1 - e^{-2\delta}} \cdot e^{-i\tau} + d \cdot e^{-\delta})\, e^{-i\int_0^y \nu_1 dy + i\frac{\pi}{4}}\right]; \qquad (24)$$

here

$$\int_{\nu_0=0}^{r} \nu_0\, dr = \int_{\nu_1=0}^{A} \nu_0\, dr + \int_A^r \frac{\nu_0 + \nu_1}{2}\, dr \pm \int_A^r \frac{\nu_0 - \nu_1}{2}\, dr$$

The $\oint$ symbol means that the integrand ν_0 and ν_1 changes abruptly at A-F from

$$\sqrt{\varphi \mp |\sqrt{\psi^2 + \alpha^2}|} \quad \text{in} \quad \sqrt{\varphi \pm |\sqrt{\psi^2 + \alpha^2}|}$$

This definition of the indentity of ν_i before and after the overlap indicates that for negative t and $(r - r_0)$, $\nu_0 < \nu_1$ and for positive t and $(r - r_0)$, ν_0 is greater than ν_1, i.e. we are following a method of notation which represents in zero approximation a real overlap. (If the other possibility is chosen: ν_0 everywhere ν_1, a continuous integrand would be obtained, but in zero approximation merely an approach of the curves. see [2] and Figure 3). Further, τ is the real value $\tau = \int_{r_0=0}^{A} \nu_0 \, dr - \int_{r_1=0}^{A} \nu_1 \, dr$ ($\tau < 0$, because $\nu_0 < \nu_1$ for negative real t). For large values of ψ / α, the factor of the first (ν_0) term becomes $\sqrt{2}$ and that of the second (ν_1) ($\alpha / \psi \sqrt{2}$). The values of ν_0 and ν_1 there are practically constant. This is also valid in (21): /399

$$e^{\pm i \int^{r} \nu_i dr} \cdot \frac{1}{\alpha} \cdot \left(\frac{d^2}{dr^2} + \varphi_0 \right) e^{\pm i \int^{r} \nu_i dr} = \frac{\varphi_0 - \nu_i^2}{\alpha} = \begin{matrix} -\frac{1}{2} \frac{\alpha}{\varphi} & i=0 \\ +2 \frac{\varphi}{\alpha} & i=1 \end{matrix} \quad \text{für}$$

Proceeding to the limit of $\psi / \alpha = \infty$, which is always possible with the resonance absent ($\alpha (r = \infty) = 0, \psi (r = \infty) > 0$), yields:

$$u_0 = \sqrt{\frac{2}{\nu_0}} \cdot \left[(c \cdot e^{-\delta} + d \cdot \sqrt{1 - e^{-2\delta}} \cdot e^{-i\tau}) \cdot e^{i \int_0^x \nu_0 dx - i \frac{\pi}{4}} \right.$$
$$\left. (c \cdot e^{-\delta} + d \cdot \sqrt{1 - e^{-2\delta}} \cdot e^{+i\tau}) \cdot e^{-i \int_0^x \nu_0 dx + i \frac{\pi}{4}} \right] \qquad (25)$$

and because of (21)

$$u_1 = -\sqrt{\frac{2}{\nu_1}} \cdot \left[(-c \cdot \sqrt{1 - e^{-2\delta}} \cdot e^{+i\tau} + d \cdot e^{-\delta}) e^{i \int_0^y \nu_1 dy - i \frac{\pi}{4}} \right.$$
$$\left. (-c \cdot \sqrt{1 - e^{-2\delta}} \cdot e^{-i\tau} + d \cdot e^{-\delta}) e^{-i \int_0^y \nu_1 dy + i \frac{\pi}{4}} \right]. \qquad (26)$$

The boundary conditions of (8a) and (8b) are the following, if in place of the Bessel functions the W.K.B. [2] approximations are used (naturally, they proceed into Bessel and Hankel functions asymptotically in ∞), and if

$$\left. \begin{aligned} \lim_{r=\infty} \left(\int_{r_0=0}^{r} \nu_0 \, dr - \int_{\mu_0=0}^{r} \mu_0 \, dr \right) &= \beta \\ \lim_{r=\infty} \left(-\int_{r_1=0}^{r} \nu_1 \, dr + \int_{\mu_1=0}^{r} \mu_1 \, dr \right) &= \gamma \end{aligned} \right| \qquad (27)$$

is

$$\lim_{r=\infty} u_0 = \sqrt{\frac{2}{\pi p_0}} \cdot \left[(\eta_0 + \tfrac{1}{2}) \cdot e^{i\beta} \cdot e^{i\int_0^x \nu_0 dx - i\frac{\pi}{4}} + \tfrac{1}{2} e^{-i\beta} \cdot e^{-i\int_0^x \nu_0 dx + i\frac{\pi}{4}} \right] \tag{28a}$$

$$\lim_{r=\infty} u_1 = \sqrt{\frac{2}{\pi p_1}} \cdot \left[\eta_1 \cdot e^{-i\gamma} \cdot e^{i\int_0^y \nu_1 dy - i\frac{\pi}{4}} \right]. \tag{28b}$$

Further, for r = 0: $\lim \nu_0 = \lim \mu_0 = \rho_0$ and $\lim \nu_1 = \lim \nu_1 = \rho_1$. If (29) and (30) is set equal to (32a) and (32b) in magnitude and derivation with respect to r (or x or y), one obtains four equations to determine the four unknowns c, d, η_0, η_1. They are found to be

$$\eta_0 = i \cdot e^{-i(2\beta + \gamma)} \cdot a^2 \cdot \sin\tau - i \cdot e^{-i\beta} \cdot \sin\beta$$

$$\eta_1 = -e^{i(\beta - \gamma)} \cdot a \cdot e^{-\delta} \cdot \sin\tau, \qquad \text{where } a = i \cdot \sqrt{1 - e^{-2\delta}}.$$

(The values of a^2, β, γ, τ are real, a^2 means $(e^{-2\delta}-1)$. The flow of the u_0 function is proportional [10]).

$2/\pi \cdot u_0' \bar{u}_0$ = real part of $(\eta_0 + \eta_0 \bar{\eta}_0) = -(1 - e^{-2\delta}) \cdot e^{-2\delta} \cdot \sin^2\tau$,

and the flow of the u_1 function proportional

$$\frac{2}{\pi} \cdot u_1' \bar{u}_1 = \eta_1 \bar{\eta}_1 = (1 - e^{-2\delta}) \cdot e^{-2\delta} \cdot \sin^2\tau.$$

Avering over τ yields for $|\eta_1|^2$:

$$\begin{cases} |\eta_1|^2 = \tfrac{1}{2} \cdot e^{-2\delta} \cdot (1 - e^{-2\delta}) \\ 2\delta = \pi \cdot T_0 = \dfrac{\alpha^2}{\psi' \nu} \cdot \dfrac{\pi}{2} \\ \nu = \dfrac{\nu_0 + \nu_1}{2}. \end{cases} \tag{33}$$

The function values of α^2, ψ', ν are evaluated at $\psi = 0$.

For values of $2\delta \ll 1$ one obtains

$$|\eta_1|^2 = \frac{\pi}{4} \cdot \frac{\alpha^2}{\psi' \nu} = \tfrac{1}{2} \cdot 2\delta \tag{29a}$$

in agreement with Landau's formula [8]. Landau, however, in his first work later integrates [8] over the $|\eta_1|^2$ in a manner which yields a substantial

[10] The values of β and γ are obviously those of Equation (27), here and in the following and not those of the step constants.

number of $|\eta_{1J}|^2$, where $|\eta_{1J}|^2 > \frac{1}{4}$, since he proceeds to J_m where at the location of the overlap

$$\nu_{J_m} = \sqrt{p^2 - \frac{J_m^2}{r_0^2}} = 0 .$$

Even the present method is no longer strictly valid when $\nu \simeq 0$, while then the discontinuity lines of $\nu_0 = 0$ intersect with those of $t = \pm i$. In any case, (29) is correct longer that (29a), because $|\eta_{1J}|^2$ is always $< \frac{1}{4}$. (The maximum of $e^{-2\delta}(1 - e^{-2\delta})$ is found at $e^{-2\delta} = \frac{1}{2}$ and amounts to $\frac{1}{4}$.) If $\delta \geq 1$, the representation of approaching curves is more suitable than the representation of overlap $|\eta_{1J}|^2$ is than equal to $\frac{1}{2} \cdot e^{-2\delta}$. Landau also obtains this other limiting value in his more recent work [13], but in another manner, which appears to be less clear to the author.

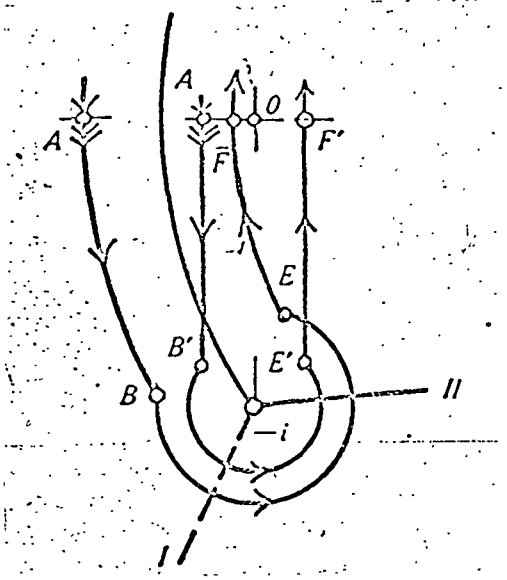

Figure 4a. $t - (\psi/\alpha)$ plane in the vicinity of $t = 0$ for nonconstant ψ' and α.

The assumption of $T(t)$ = constant, which is employed in Figure 4, incidentally is not necessary. It is only required to approximate $T(t)$ in the area desired as analytical functions of t, different from t. For

$$\int t\,dt/(1+t^2) \quad \text{and} \quad \int dt/\sqrt{1+t^2}$$

A' or F' is chosen in place of A and F as the lower limit (see Figure 4a) and the path of A' - B', etc. is described, while for

$$\int dt \cdot T(t) \cdot \sqrt{1+t^2}$$

the old path A-B..., now deformed, is employed. /402

10. The Link Method of the Approximation Function for Case I (on the real axis everywhere > 0).

Let no overlap occur in case I in the entire real velocity range on the real axis. It will then be seen that the vicinity where $W_{01}^I = \frac{1}{2}(E_0 - E_1)$, i.e. where $|\alpha| = \psi$, has properties similar to the location of overlap in the preceding paragraph. This is understandable, because there the potential energy

curves for $\alpha = 0$ (corresponding to μ_1^2 and μ_2^2 in Equation (17) in paragraph 7) begin to differ significantly from those for $\alpha \simeq \psi$ (corresponding to ν_0^2 and ν_1^2 in Equation (17) in paragraph 7). The latter curves (ν_0^2 and ν_1^2) there already are at twice the level distance $2\sqrt{\psi^2 + \alpha^2} \cong 2\sqrt{2}\,\psi^2$ as the undisturbed curves. For smaller distances, where $|\alpha| > \psi$, the distance in level grows with 2α and for greater distances of the atoms ($\alpha \to 0$) is becomes constant $= 2\psi$. The potential energy curves thus lose their meaning in both versions in this area (ν_i or μ_i) identification. The image somewhat resembles that of the preceding paragraph if α and thus δ is allowed to grow very large so that the Neumann-Wigner representation of the approach becomes more advantageous than intersection. This is the meaning of the identification of curves mentioned at the end of paragraph 9 in parenthesis. The final result of the present paragraph again becomes very similar to that of the preceding paragraph if it is assumed that α and ψ have changed roles. This is also indicated by the fact that the present derivation cannot be accomplished in the t plane, which roughly resembles the r plane, but that even initially the abstract value of z, reciprocal to t, must be employed. Let us use the form (23) of the solution of paragraph 8. The point $z = \alpha / \psi = 0$ than corresponds to the location of $r = \infty$. The points $z = \pm i$ are treated as above and the discontinuities are determined:

$$\arg\left(\pm i \int_{\pm i}^{z} Z(z) \cdot \sqrt{1 + z^2} \cdot dz\right) = \pi; \quad Z = \frac{\psi}{2\nu z'}; \quad \nu = \frac{\nu_0 + \nu_1}{2}.$$

However, case I cannot be treated in the general manner of case II. The interaction energies $W_{01}^{I} = (h^2/8\pi \cdot M) \cdot \alpha(r)$ must be considered more exactly. The change in electron configuration from $\Phi_0 = \chi_0$ to $\Phi_1 = \chi_1$, for $r = \infty$, yields the criterion for a completed collision. χ_0, however, means: atom I in condition m, atom II in condition n. χ_1 in a similar manner: atom I in condition m', atom II in condition n'. The interaction energy W_{01}^{I} can than be developed in many cases for large distances following powers of 1/r. The first term for mutually neutral systems is

$$\frac{d_I \cdot d_{II}}{r^3},$$

the second term

$$\frac{d_I \cdot q_{II} + q_I \cdot d_{II}}{r^4}$$

etc., where d_1, q_1, etc. is the dipole momentum and quadrupole momentum associated with the mm' transition of atom I and correspondingly of atom II. For optically permissible transitions, the term with $1/r^3$ will be decisive at large distances, etc. This result is obtained through classical considerations. (Details concerning the wave-mechanical justification are found in the first paper of Morse and the author [6], paragraph 3.) Let us restrict ourselves in the following to functions α, which for large r behave as $\varepsilon \cdot r^{-(\lambda+1)}$, where $\lambda \geq 2$.

Then, if

$$\nu = \frac{\nu_0 + \nu_1}{2}$$

and if ψ is constant in the range of $|z| < 2$:

$$\alpha' = -(\lambda+1)\cdot\frac{1}{r}\alpha;\quad r = \left(\frac{\varepsilon}{\alpha}\right)^{\frac{1}{\lambda+1}}$$

or

$$z' = -\frac{\lambda+1}{r}\cdot z = -(\lambda+1)\cdot\frac{\psi^{\frac{1}{\lambda+1}}\cdot z^{1+\frac{1}{\lambda+1}}}{\varepsilon^{\frac{1}{\lambda+1}}}.$$

Let us set $n = 1 + 1/(\lambda+1)$ and obtain

$$Z(z) = -\frac{\psi^{1-\frac{1}{\lambda+1}}}{(\lambda+1)\cdot\varepsilon^{\frac{1}{\lambda+1}}}\cdot\frac{1}{z^n};\quad 1 < n < 1.5.$$

The z plane, since n is not an integer, must be interpreted as a Riemann surface cut along the negative real axis. The directions of the discontinuities may be determined if $z = |z|\cdot e^{i\vartheta}$, $z-(+i) = \varrho\cdot e^{i\varphi}$, /404

$$z-(-i) = \tau\cdot e^{i\psi} \quad \text{und} \quad dz = |dz|\cdot e^{i\varphi'} \text{ ist,*)}$$

from

$$\arg\left(\pm i\int_{z=+i}^{r}\frac{\nu_0-\nu_1}{2}dr\right) = \arg\left[\mp i\int_{+i}^{z}\frac{dz}{z^n}\cdot(z-(+i))^{\frac{1}{2}}\cdot(z-(-i))^{\frac{1}{2}}\right] = \pi + m\cdot 2\pi$$

or, if $\lambda\neq$ means the argument of $\pm i\int_{+i}^{r}(\nu_0-\nu_1)\,dr/2$.

$$\lambda_{\mp} + \varphi' = \pi + m\cdot 2\pi,$$

where $\lambda_{\mp} = \frac{1}{2}\cdot(\varphi+\psi-2n\vartheta \pm \pi)$ [11]

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* See note on page 390.

11. λ^+ and λ^- should not be confused with the λ exponent without index in $\alpha = \varepsilon\cdot r^{-(\lambda+1)}$.

Let us set $0 < \varphi, \psi < 2\pi$, and on the zero sheet of the Riemann surface $-\pi < \vartheta < \pi$. For the initial directions $\varphi' = \varphi \equiv \varphi_0$ must be selected. This results for φ_0, because $\vartheta_0 = \psi_0 = \pi/2$: for D_+ and C_- steps (λ_-) in: /405

$$\varphi_0 = \frac{1 + 8m + 2n}{6}\pi.$$

A visual representation is given for $\alpha = \epsilon/r^2$, $\lambda = 1$ and $n = 1.5$, in Figure 5: if φ_0 is designated, for D_+ steps and $m = 1$, by

$$\varphi_0 = 2\pi - \sigma, \text{ and } \sigma = \frac{2n - 3}{6}\pi > 0$$

then $\sigma = 0$ for $n = 1.5$. The semicircle $|z| = 1$ of $-\pi/2 < \vartheta < \pi/2$ satisfies the equation, because there $\varphi + \psi = 3\pi/2 + 2\psi$, and $\psi = \vartheta/2 + \pi/4$. Therefore, $\varphi + \psi = 2\pi + \vartheta$ and $\lambda_- = 3\pi/2 + \vartheta$. The tangent is, however, in all points $\varphi' = 3\pi/2 - \vartheta$, so that $\lambda_- + \varphi' = \pi + 2\pi$. The curve $\lambda_- + \varphi' = \pi$, at the steps of C_- and D_+ (I) proceeds to $z = \infty$ in asymptotic direction $\varphi'_\infty = \pi$. Curve $\lambda_+ + \varphi' = \pi$ where C_+ and D_- steps (II) is close to $z = 0$ from the direction of $\vartheta_\infty = \pi$. Both I and II may be crossed therefore at a location where

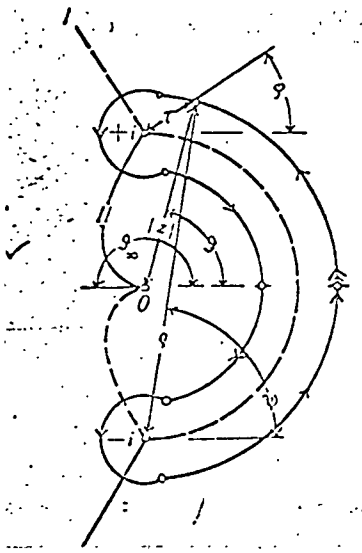

Figure 5. The z-(α/ψ) plane in the vicinity of $z = 0$ for constant ψ and $\alpha = \epsilon/r^2$. The z plane represents a Rieman surface cut open along the negative real axis.

$$\pm i \int_{z=i}^{r} \frac{\nu_0 - \nu_1}{2}\, dr$$

grows past all limits if the points ν_1 and $\nu_0 = 0$ are far distant. The relationships around the point $-i$ represent a mirror image[12], as can be shown readily. For the determination of the step constants, the path of A-B-E-F-G-H-A[13] is again selected.

Since we are interested in solving $\lim r = \infty$, that is, $\lim z = +0$, we select the path A-B-E-F for the connecting method after stepconstants are determined.

If $\alpha = \epsilon/r^{\lambda+1}$ and $\lambda > 1$, $1 < n < 1.5$, the situation changes only slightly (Figure 6). The semicircle becomes a curve K_w, which departs from point i under an angle $2\pi - \sigma$ ($\sigma = (2n - 3)\pi/6 > 0$). Let us plot the circle K_a for $\sigma = 0$ from

12. Mirror image in the sense that the curves behave like a mirror image, but that I and II interchange their roles if the path indicated (Figure 5) is taken.

13. For clearness sake, the letters A-B...F are not shown in Figure 5, only the points and the path indicated by a closed, feathered arrow (as in Figure 4).

Figure 5, in Figure 6 and another circle K_i, which in the points $z = \pm i$ has the same tangent direction as K_w ($2\pi - \sigma$ or $3\pi - \sigma$). /406

If φ_i' and φ_a' is used to designate the tangential directions of the circles Ki and K_a as functions of $\vartheta (\pi/2 > \vartheta > -\pi/2$, and if φ' indicates the direction as obtained from $\lambda_- + \varphi' = 3\pi$, then:

$$\varphi' - \varphi_i' = 3\sigma\left[\frac{1}{2\sigma}\sin^{-1}(\sin\sigma\cdot\sin\vartheta) - \frac{\vartheta}{\pi}\right]$$

$$\simeq 3\sigma\left[\frac{\sin\vartheta}{2} - \frac{\vartheta}{\pi}\right] > 0$$

and

$$\varphi' - \varphi_a' = -3\sigma\left[\frac{\vartheta}{\pi}\right] < 0.$$

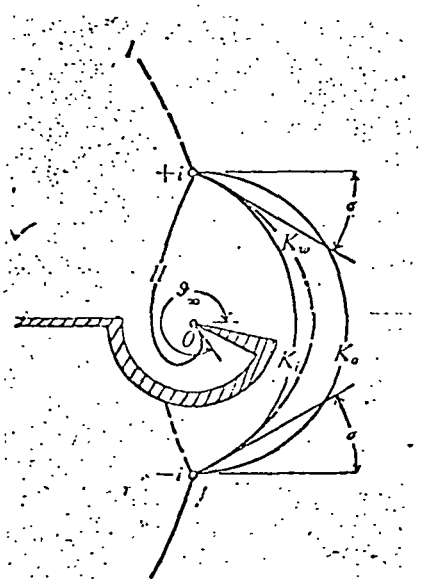

Figure 6. The z-(α/ψ) plane in the vicinity of z = 0 for $\alpha = \varepsilon / r^{\lambda+1}$, ($\lambda > 1$). The z plane is a Riemann surface cut open along the negative real axis. In the figure the zero sheet ($-\pi < \vartheta < +\pi$) and a section of the + first sheet ($+\pi < \vartheta < 3\pi$) are shown. The shaded area represents the section.

The true K_w curve, on which $\varphi' - \varphi_w' \overset{id}{=} 0$, must therefore between K_i and K_a and, since the absolute value of the first expression is everywhere less than that of the second, close to K_i. Curve I still proceeds into the infinite with an asymptotic direction of $\varphi_\infty = (n - \tfrac{1}{2})\pi$. Curve II approaches helically on the Riemann surface the point z = 0 with the asymptotic direction

$$\vartheta_\infty = \frac{\pi}{2}\cdot\frac{1}{n-1} = (\lambda+1)\cdot\frac{\pi}{2}.$$

/407

Step constants and the link are determined as in case II. After phase averaging, one again obtains for $|\eta_1|^2$:

$$|\eta_1|^2 = \tfrac{1}{2}\cdot e^{-2\delta}\left(1 - e^{-2\delta}\right)$$

$$\delta = \left|i\int_{-i}^{+i} Z(z)\cdot\sqrt{1+z^2}\cdot dz\right| = \frac{\psi^2}{2\nu\alpha'}\cdot M_\lambda$$

where α' is the absolute value of the derivation of α from the location $\alpha^2 = \psi^2$ and where

$$M_\lambda = \left|i\int_{-i}^{+i}\frac{1}{z^{1+\frac{1}{\lambda+1}}}\cdot\sqrt{1+z^2}\cdot dz\right|$$

is a number of the order of magnitude 1. (For $\lambda = 1$ the value is 3.41). Then

$$|\eta_1|^2 = \frac{1}{2}\cdot\left(e^{-M_\lambda \frac{\psi^2}{\nu a^2}} - e^{-2M_\lambda \frac{\psi^2}{\nu a^2}}\right). \tag{30}$$

This relationship is valid only if in the range where $|\alpha| \cong |\psi|$, ν is real and nearly constant, i.e. if $\nu_0 = 0$ is far distant. As an approximation, (34) is valid wherever $|\alpha_{max}| > |\psi|$.

As noted in the introduction of the present paragraph, Equation (30), except for the numerical factor M, corresponds exactly to Equation (29), if the meaning of α and ψ is interchanged.

11. Estimation of Matrix Elements $|\eta_{1J}|^2$ by the Perturbation Method

If the conjugation is very weak, the transition probabilities determined by the link method ($|\eta_{1J}|^2$, (29)) in Paragraph 9 and (30) in paragraph 10, should pass into the values determined by the perturbation theory (14), paragraph 6.

In case I this transition cannot be observed, because the derivation given in paragraph 10 is valid only for the case where $|\alpha_{max}| > |\psi|$. Here, however, the conjugation is not very weak.

If $|\alpha|$ is $> |\psi|$ over the entire velocity range, then, at least for large values of J, approximately

$$r_i = u_i \cong \sqrt{r}\cdot J_J(p_i r).$$

If one is restricted again to $\alpha = \varepsilon\cdot r^{-(\lambda+1)}$ and if $\rho_1 < \rho_0$, then (14) is valid: /408

$$\eta_{1J} = \frac{\pi\varepsilon}{2}\int_0^\infty \frac{J_J(p_0 r)\cdot J_J(p_1 r)\cdot dr}{r^\lambda} = \frac{\pi\varepsilon}{2}\,\frac{1}{2^\lambda\cdot\Gamma\left(\frac{\lambda+1}{2}\right)}$$

$$\cdot\frac{\Gamma\left(J-\frac{\lambda-1}{2}\right)}{\Gamma(J+1)}\cdot\left(\frac{p_1}{p_0}\right)^J\cdot F\left(-\frac{\lambda-1}{2},\ J-\frac{\lambda-1}{2},\ J+1,\ \left(\frac{p_1}{p_0}\right)^2\right).$$

Let us use Stirling's formula (large J-s) for the Γ functions and let us set

$$F \cong \left[1 - \frac{J}{J+\left(\frac{\Gamma(\lambda)}{\Gamma\left(\frac{\lambda+1}{2}\right)}\right)^{\frac{2}{\lambda-1}}}\cdot\left(\frac{p_1}{p_0}\right)^2\right]^{\frac{\lambda-1}{2}},\qquad c_1 = \frac{\pi^2\cdot\Gamma(\lambda)^2}{4^{\lambda+1}\cdot\Gamma\left(\frac{\lambda+1}{2}\right)^4}$$

$$c_2 = \left[\frac{\Gamma\left(\frac{\lambda+1}{2}\right)}{\Gamma(\lambda)}\right]^{\frac{2}{\lambda-1}}$$

then

$$|\eta_{1J}|^2 = c_1 \cdot \varepsilon^2 \left[p_0^{2\lambda-2} \cdot \frac{1}{J^{2\lambda}} \right] e^{-\frac{\psi}{p_0^2} J} \cdot \left[1 + c_2 \cdot \frac{\psi}{p_0^2} J \right]^{\lambda-1} \quad (31)$$

Let us now set $\alpha_{max} = \varepsilon \cdot p_0^{\lambda+1} / J^{\lambda+1}$

and

$$\left| \alpha'_{max} \right| = \left| \frac{\lambda+1}{r_{min}} \cdot \alpha_{max} \right| = \left| \frac{(\lambda+1)\, p_0}{J} \cdot \alpha_{max} \right|$$

then

$$\frac{\psi}{p_0^2} J = \frac{\psi \alpha_m}{p_0 \alpha'_m} (\lambda+1)$$

(α_m and α'_m always indicate absolute values, m means maximum).

Then, with good approximation for $|\alpha_{max}| < |\psi|$:

$$|\eta_{1J}|^2 = c_1 \cdot \left[\frac{\alpha_m^{\lambda}}{p_0 \alpha'_m} (\lambda+1) \right]^2 \cdot e^{-\frac{\psi \alpha_m}{p_0 \alpha'_m}(\lambda+1)} \cdot \left[1 + c_2 \cdot (\lambda+1) \frac{\psi \alpha_m}{p_0 \alpha'_m} \right]^{\lambda-1} \quad (31a)$$

The smaller the ψ/α', the larger the $|\eta|^2$, as also required by London [7]. /409

Let us designate now for the partial wave J, where

$$\alpha_m = |\alpha(r_{min})| = \psi,$$

$r_{min} = \rho_1^{-1}$ with r_0 and the J by J_m.

The value of $J = J_m$ therefore is associated, in accordance with the dissociation into spheric harmonics performed in paragraph 3, with the partial wave corresponding to an approach of atom centers to the point where the perturbation energy becomes equal to the resonance uncertainty.

For the η_{1J}^2, where $J > J_m$, in (31a) the characteristic exponential function is

$$\exp\left[-(\lambda+1) \frac{\psi \alpha_m}{p_0 \alpha'_m} \right],$$

while for $J < J_m$, where $\alpha_m > \psi$, in (30) of paragraph 10, it becomes

$$\exp\left[-M_\lambda \frac{\psi \psi}{p_0 \alpha'_m} \right].$$

It appears therefore, as if, aside from the numerical factors M_λ and $\lambda + 1$, the α_m, which grows with decreasing values of J, in the nominator would increase only to the value of $\alpha_m = \psi$ ($J = J_m$) and then remain constant, while the α'_m

in the denominator keeps on increasing. This phenomenon can be made plausible in another, if less strict manner, also:

If α is idealized, by setting $\alpha = \alpha' \cdot (r_0 - r) = \alpha' \cdot x$ and $\alpha = 0$ for $r > r_0$, then in the vicinity of $r < r_0$:

$$v_0 v_1 = \frac{2}{\pi} \frac{1}{\sqrt{\nu_0 \nu_1}} \cdot \frac{1}{2} \left[\cos \left\{ \int_0^x (\nu_0 - \nu_1)\, dx \right\} \cdot \cos \tau + \sin \left\{ \int_0^x (\nu_0 - \nu_1)\, dx \right\} \cdot \sin \tau \right] \tag{32}$$

and a rapidly oscillating part with

$$\begin{matrix} \cos \\ \sin \end{matrix} \left\{ \int_0^x (\nu_0 + \nu_1)\, dx \right\}.$$

τ is a phase constant (see paragraph 10), which here is immaterial.

For $\sqrt{\psi^2 + \alpha^2}\ \mathrm{tg}^{-1}\ \alpha/\psi$ let us set (see paragraph 7) $\alpha \cong \alpha' \cdot x$. <410

The equal setting of

$$\int_0^x (\nu_0 - \nu_1)\, dx = \frac{\alpha'}{\nu} \int_0^x \sqrt{\frac{\psi^2}{\alpha'^2} + x^2} \cdot dx = \frac{\alpha'}{2\nu} \cdot x \cdot \sqrt{\frac{\psi^2}{\alpha'^2} + x^2} = \frac{\psi^2}{4 \nu \alpha'} \cdot t$$

is permissible if the logarithmic terms are neglected.

$$\alpha' \cdot x\, dx = \frac{\psi^2}{2\alpha'} \cdot \frac{t\, dt}{\sqrt{1 + t^2}},$$

Then, based on (19) in paragraph 7:

$$|\eta_{1J}|^2 = \frac{\psi^2}{4 \nu \alpha'} \cdot \int_0^\infty \frac{t\, dt}{\sqrt{1 + t^2}} \begin{matrix} \cos \\ \sin \end{matrix} \left[\frac{\psi^2}{4 \nu \alpha'} \cdot t \right] \cong e^{-\frac{\psi^2}{4 \nu \alpha'} + \log \cdot \mathrm{Gl.}} \tag{33}$$

The exponent $\psi^2/4\,\nu\alpha'$ thus appears with respect to order of magnitude, but it is not known at which point α' should be taken (with a nonconstant α').

Finally, let us mention, for the sake of completeness, Landau's [8] matrix element. It is obtained from (19a) and (21) if one considers that for $x = 0$: $\psi = \psi' \cdot x$, where in (32) u_i should be set in place of v_i and μ_i in place of ν_i (the phase constants are, however, different from those of paragraph 9, due to the difference between ν_i and μ_i).

$$\int_0^x (\mu_0 - \mu_1)\, dx = \frac{\psi'}{2\mu} \cdot x^2$$

and that

$$\int_0^\infty \begin{matrix}\cos\\ \sin\end{matrix}\left[\frac{\psi'}{2\mu}x^2\right]\cdot dx=\left[\frac{2\pi\mu}{\psi'}\right]^{\frac{1}{2}}.$$

Then, after communication by way of the phase

$$|\eta_{1J}|^2=\frac{\pi}{4}\frac{\alpha^2(r_0)}{\mu_J(r_0)\cdot\psi'(r_0)};\ \psi(r_0)\neq 0 \tag{34}$$

This evaluation by Landau is obviously permissible only if $|\eta_{1J}|^2 \ll \frac{1}{4}$. In the resonance case, i.e. for very small $\psi'(r_0)$ and for large α^2 and small μ_J the result is not valid. Equation (34) is identical with (29a) (since for small α and large ψ' $\mu_i = \nu_i$). /411

12. Determination of the Effective Cross Section in Case I (No intersection of curves)

In case I the effective cross section divides into two parts. Let us replace the summation $\sum_J$ J by $\int$ JdJ. For $J \ll J_m$ (if $J_m/\rho_1 \cong r_0$ and if $\alpha(r_0) = \psi$) Equation (30) is certainly valid. We have no valid expression for $J \cong J_m$, because for $J \cong J_m$ and $J > J_m$ the discontinuity lines of $\nu_1 = 0$ and of $z = \pm i$ are intersecting in the infinite. However, in any case, the expression remains in the same order of magnitude. Certainly, for $J \gg J_m$ Born's[6] (or London's [7]) because they coincide) approximation of (31) or (31a) is valid. If one applies (30) and (31a) to $J = J_m$, no great error is committed.

Therefore (35)

$$q = q_< + q_>, \quad \text{where} \lesssim : J \lesssim J_m \text{ means} \tag{35}$$

For the $q_<$ part let us consider only the case of "good" resonance, i.e. let us set in place of r_0

$$r_0 = J_m/p_m;\ (p_m^2 = p_0^2 - 8M\pi^2\cdot W_{00}(r_0)/h^2)$$

$$\nu_0^2 \cong \nu_1^2 \cong \left[\frac{\nu_0+\nu_1}{2}\right]^2 \simeq \nu^2 \cong p_m^2 - \frac{J^2}{r_0^2},$$

so that ν^2 ($J = J_m$) = 0 at $r = r_0$. 14

Let us introduce the values of

$$z=\frac{1}{\sqrt{1-\frac{J^2}{p_m^2 r_0^2}}},\quad k=3\frac{\psi^2}{p_0\alpha}$$

14. The factor M_λ of Paragraph 10, which for $\lambda = 2$ is 3.41, has been set equal to 3 in the following for simplicity's sake.

and define the function

$$f_1 = 2\left[\int_1^\infty \frac{dz}{z^3}\left(e^{-kz} - e^{-2kz}\right)\right]$$

then

$$q_< = \pi r_0^2 \cdot 2\left[\frac{p_m}{p_0}\right]^2 \cdot f_1\left(3 \cdot \frac{\psi^2}{p_m \alpha'}\right). \tag{36}$$

The function $f_1(k)$ increases for $k < 1$ as does $2k$, reaches a flat maximum of 0.22 at $k = 0.45$ and approaches for large values of k the function $2 \cdot e^{-k}/k$. /412

Let us set $z = J/J_m$ for the $q_>$ part, then, from (31):

$$q_> = \pi r_0^2 \cdot 8 c_1 \left[\frac{\psi}{p_0^2} J_m\right]^2 \cdot \sum_{k=0}^{k=\lambda-1} \binom{\lambda-1}{k} \cdot c_2^k \cdot \left[\frac{\psi}{p_0^2} \cdot J_m\right]^k \cdot \int_1^\infty \frac{dz}{z^{2\lambda-1-k}} \cdot e^{-\frac{\psi}{p_0^2} J_m \cdot z}.$$

It is seen that for poor resonance

$$\frac{\psi^2}{p_0^2 \alpha'} \gg 1,$$

$q_>$ is preponderant, because in $q_>$ the exponential function is multiplied by the large number

$$\left(\frac{\psi}{p_0^2} J_m\right)^2$$

while in $q_<$ the large number

$$k = \left(\frac{\psi}{p_0^2} J_m\right) = 3\frac{\psi^2}{p_0 \alpha'}$$

occurs in the nominator.[15]

A general discussion would grow too extensive. Let us therefore consider the specific case of $\alpha = \epsilon/r^3$, $\lambda = 2$.

---

15. $q_>$ is nothing but the cross section calculated by Morse and the author [6] if the β of the loc. cit. is set equal to J_m and $W/E = 2\ \psi/p_0^2$. On the curves of the figures D (W/E) in paragraph 5 of the earlier work this means that with increasing resonance, curves with higher β must be used. The calculation shows, however, that $J_m = \beta$ easily exceeds the order of magnitude of 100. The "resonance curves" thus become flatter. The value of $q_<$, which increases with sharper resonance, must, however, be added; it cancels out this effect and finally prevails.

Let us define the functions f_3 and f_4 as

$$f_3(k) = 2\int_1^\infty \frac{dz}{z^3} \cdot e^{-k\cdot z} = e^{-k} - k\cdot\{e^{-k} - k[-Ei(-k)]\};$$

$$[-Ei(-k)] = \int_k^\infty \frac{e^{-u}}{u}\,du$$

and

$$f_4(k) = \int_1^\infty \frac{dz}{z^2} \cdot e^{-kz} = e^{-k} - k[-Ei(-k)].$$

Then:

/413

$$f_1(k) = f_3(k) - f_3(2k)$$

$$\tfrac{1}{2}\lim_{k=\infty} f_1(k) = \tfrac{1}{2}\lim_{k=\infty} f_3(k) = \lim_{k=\infty} f_4(k) = \frac{1}{k}\cdot e^{-k}$$

$$f_3(0) = f_4(0) = 1;\ \lim_{k=0} f_1(k) = 2k.$$

Because of

$$\lambda + 1 = 3:\ c_1 = 1/4;\ c_2 = \pi/4 \quad \text{(see (31))}$$

$$q_> = \pi r_0^2 \cdot 2 \cdot \left(3\frac{\psi^2}{p_0\alpha'}\right)^2 \cdot \left[\tfrac{1}{2}\cdot f_3\left(3\frac{\psi^2}{p_0\alpha'}\right) + \frac{\pi}{4}\left(3\frac{\psi^2}{p_0\alpha'}\right)\cdot f_4\left(3\frac{\psi^2}{p_0\alpha'}\right)\right] \tag{37}$$

or, from (36), if $\rho_m \sim \rho_0$ and from (37)

$$q = \pi r_0^2 \cdot \left[2f_1(k) + k^2\cdot f_3(k) + \frac{\pi}{2}k^3\cdot f_4(k)\right]$$

$$k = \frac{\psi}{p_0^2}J_m = \frac{\psi^{\frac{5}{3}}\cdot\varepsilon^{\frac{1}{3}}}{p_0},\ \text{da}\ r_0 = \left(\frac{\varepsilon}{\psi}\right)^{\frac{1}{3}}\ \text{ist.} \tag{38}$$

In Figure 7, the expression in parentheses (solid line) and the first sum (broken line) are plotted. The first sum, which prevails in the case of good resonance, represents the $q_<$ component while the difference between the solid and the broken line indicates the $q_>$ component. For small values of k:

$$q = \pi r_0^2 \cdot 4k \tag{39}$$

and for large values of k:

$$q = \pi r_0^2 \cdot \frac{\pi}{2}k^2\cdot e^{-k} \tag{40}$$

If $\lambda \neq 2$, (39) is still valid, while in (40), the numerical value of the factor $\pi/2$ changes into $8\ c_1\ c_2^{\lambda-1}$ and k takes the place of k^2. k in (39) has the following meaning: $M_\lambda \psi^2/\rho_m$ ' and in (40): $(2+1)^2/\rho_m x'$.

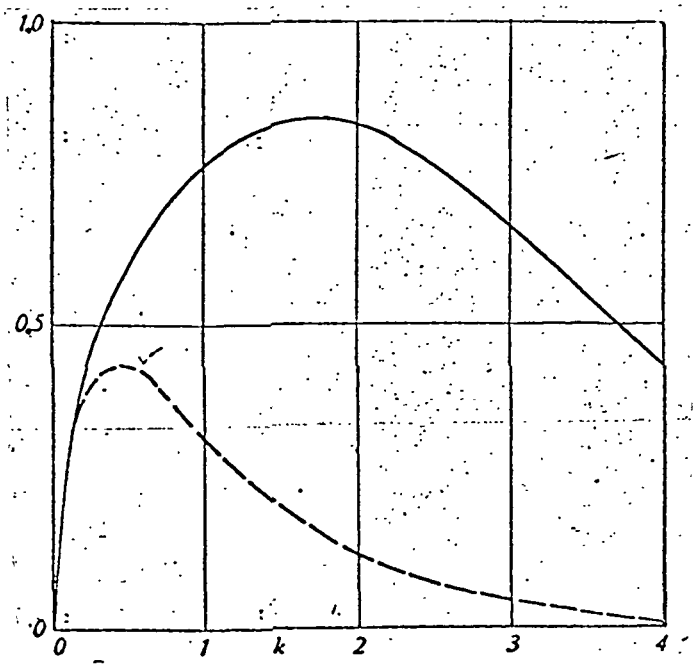

Figure 7. The function $2f_1(k)$ is drawn with a broken line (---) of Eq. (36) and the sum in Eq. (38) $[2f_1(k) + k^2 \cdot f_3(k) + \pi k^3 \cdot f_4(k)/2]$ with a solid line (____). The sum behaves for very small k as 4k and for very large k as $\pi k^2 \cdot \exp(-k)/2$.

The formulas of (29) and (30) were obtained from the solutions of the differential equation (18a) or (20) and the boundary conditions (28a) and (28b). It was assumed that r = + real ∞ corresponds to a point t = + real ∞ for case II, and z = + real 0 in case I, which is located far from the discontinuity line connecting +1 with -1, and also from z (Or t) = $\pm i$. "Far" /414 here means that

$$\left| i \int_{z,t=\pm i}^{r} (\nu_0 - \nu_1)\, dr \right|$$

is a large number. This is always the case if $\nu_0 \neq \nu_1$ for r = ∞, i.e. if $\psi_\infty \neq 0$. Then

$$\lim_{r=R=\infty} \left| i \int_{z,t=\pm i}^{r} (\nu_0 - \nu_1)\, dr \right| > \left| \int_0^{\infty} \frac{\psi_\infty}{p_0}\, dr \right| > \frac{\psi_\infty}{p_0} \cdot R$$

where R is the maximum distance, i.e. our considerations always refer to lim R = ∞.

Equation (39) is thus valid for arbitrarily small ψ_∞ and therefore for small k, as long as

$$\lim_{R=\infty} \frac{\psi_R \cdot R}{p_0} = \infty .$$

Let us designate this case for arbitrarily small ψ_∞ as the limiting case, in contrast to the resonance case discussed in paragraph 13. /415

In the limiting case thus:

$$\lim q = \frac{12\pi \cdot \psi_\infty^{1-\frac{3}{1+\lambda}} \cdot \varepsilon^{\frac{3}{1+\lambda}}}{p_0 \cdot (\lambda+1)} .$$ 16

16. Strictly speaking, 4 M is in place of 12.

In the case of the sharpening resonance, arbitrarily large values are obtained for $\lambda + 1 < 3$.

For $\lambda + 1 = 3$ (the case under consideration), q tends toward a definite limiting value. The limiting cross section of $\lambda + 1 = 3$ is of the same order of magnitude as the maximum cross section of $\lambda + 1 > 3$ (see below for $\lambda + 1 > 3$).

For $\lambda + 1 > 3$, q passes through a maximum with decreasing ψ_∞. There the parenthetical expression $[2f_1 + \ldots]$, which is analogous to (38), is of the order of magnitude of 1. The maximum thus is approximately

$$q_{max} = \pi r_{00}^2 \times 1.$$

The result is valid for all interactions where $\lambda + 1 > 3$. The values of $r_{00}(k_0)$ and k_0 are determined by

$$\frac{d}{dk}\left\{\left[2 \cdot f_1(k) + k^2 \cdot \sum_i c_i k \cdot f_{3+i}\left(\frac{3}{\lambda+1}\right)\right] \cdot r_0(k)\right\} = 0$$

k_0 also is of the order of magnitude of 1, so that the order of magnitude of r_{00} is determined by

$$\alpha'(r_{00}) = \frac{\psi^2}{p_m}$$

The limiting cross section here is = 0.
In general:

The velocity dependence is given only the parenthetical expression (Figure 7, for $\lambda = 2$), because r_0 is constant and k proportional to $1/\rho_0$. The effective cross section thus attains a maximum of πr_0^2 for $\rho_0 = \psi^2/\alpha'(r_0)$ and then declines with $1/\rho_0$ to zero.

The order of magnitude of effective cross sections attains the level of gas kinetic cross sections and even exceeds them.

Figure 8 (Curve a) presents a "resonance curve" for the case of

$$T_0 = .1 \text{ Volt}, \quad U_{01}^{-1} = \frac{(e a_0)^2}{r^3},$$

where $M = 10\ M_N$ (e = electron charge, a_0 Bohr's orbital radius, M_H mass of the atomic weight 1).

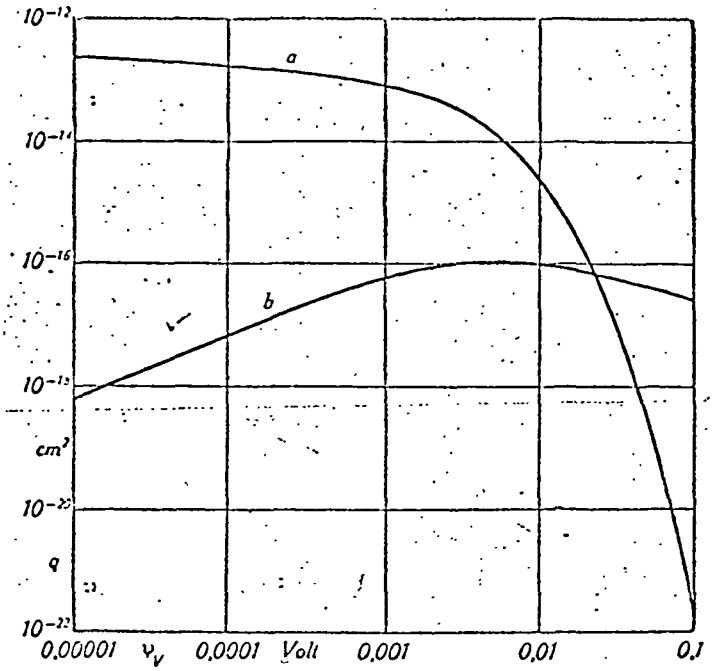

Figure 8. Effective cross sections for collisions of the second kind between atoms on a log scale: q in cm^2 against ψ_V in volt. Curve a is calculated for nonintersecting potential curves (Case I) with an interaction of $W^I = (ea)^2/r^3$. Curve b for intersecting potential curves with $\psi'_V = \psi_V 10^{-8}$ volt cm^{-1} and with an interaction energy $W^{II} = h^2 \Lambda J/8\pi^2 Mr^2$ ($\Lambda = 1$). Relative velocity is in both cases is one electron volt and the reduced mass ten times the mass of atomic weight one.

13. Effective Cross Section in the Case of Resonance

The values of $|\eta_1 J|$ were derived in paragraph 9 and 10 by assuming that

$$\lim_{r=\infty} \frac{\psi(r) \cdot r}{p_0} = \infty$$

For $\psi_\infty = 0$ therefore a series of different cases is obtained, according to the limiting case toward which $\psi \cdot r/p_0$ tends. The preceding paragraph treated the limiting case of $\psi \cdot R = \infty$.

London [7] considers the resonance case of indentical systems: ψ identically = 0. The conjugated equations (18a) dissociate into two nonconjugated ones, if the functions $u_0 + u_1$ and $u_0 - u_1$ are introduced. His result, using the phase constants β and γ (Equation 27, Paragraph 9) (since no intersection is permissible in the finite range, then $\int = \int$): 417

$$|\eta_1 J|^2 = \frac{1}{4} \cdot \sin^2(\beta + \gamma). \tag{41}$$

This equation can be proven in a more general manner. Let us not require the identical disappearance of ψ, but merely that

$$\lim_{r=\infty} \frac{\psi}{\alpha} = \lim_{r=\infty} t = 0$$

Let us consider e.g. our Equation (22) as a solution of (20), where it is known that $c_{\pm} = c \cdot \exp(\mp i\pi/4)$ and $d_{\pm} = d \exp(\mp i\pi/4)$. Let the lower limit of the ν_i integrals be = 0 and that of the t integrals t = 0. Then, for small $t = \psi/\alpha$:

$$\lim_{r=\infty} u_0 = \nu_0^{-\frac{1}{2}} \cdot c \cdot \left(1 + \tfrac{1}{2}\frac{\psi}{\alpha} \ldots\right) \cos\left(\int^r \nu_0\, dr - \frac{\pi}{4}\right)$$
$$+ \nu_1^{-\frac{1}{2}} \cdot d \cdot \left(1 - \tfrac{1}{2}\frac{\psi}{\alpha} \ldots\right) \cos\left(\int^r \nu_1\, dr - \frac{\pi}{4}\right).$$

From Equation (21), one obtains, since for

$$t = 0\text{: } \lim \frac{\varphi_0 - \nu_0^2}{\alpha} = -1,\ \lim \frac{\varphi_0 - \nu_1^2}{\alpha} = +1 \text{ ist:}$$

$$\lim_{r=\infty} u_1 = -\nu_0^{-\frac{1}{2}} \cdot c \cdot (1 - \ldots) \cos\left(\int^r \nu_0\, dr - \frac{\pi}{4}\right)$$
$$+ \nu_1^{-\frac{1}{2}} \cdot d \cdot (1 + \ldots) \cos\left(\int^r \nu_1\, dr - \frac{\pi}{4}\right).$$

Let us observe that $\nu_0 = \nu_1$ for $r = \infty$ and let us set

$$\tau = \int_{r_0=0}^{t=0} \nu_0\, dr - \int_{r_1=0}^{t=0} \nu_1\, dr,$$

then, by satisfying the boundary conditions of (28 a, b):

$$|\eta_{1J}|^2 = \frac{1}{4} \sin^2 \tau.$$

If ψ is identically 0, then μ_0 becomes identically equal to μ_1 and in accordance with Equation (27) $\tau = \beta + \gamma$.

In the special case of $\psi^{id} = 0$ and $\alpha = \epsilon/r^2$ one obtains for

$$|\eta_{1J}|^2 = \frac{1}{4} \sin^2 \left(\sqrt{J^2 + \epsilon^2} - \sqrt{J^2 - \epsilon^2}\right)\pi.$$

For large J, this becomes $= \pi^2/4\ \epsilon/J^2$ (as also yielded by matrix evaluation) so that

$$q \infty \sum_J |\eta_{1J}|^2 \cdot J$$

does not converge. In the case of $\lambda \geq 1$ thus the effective cross sections converge neither in the limiting case (Paragraph 12) nor in the resonance case. The fact that the resonance case $\psi R = 0$ behaves differently from the limiting case $\psi R = \infty$, is also shown by the work of London:

His ω function (designated by g in the present paper, in paragraph 7) performs a phase step during the transition from $\psi R = \infty$ to $\psi R = 0$.

With the exception of identical systems, in our opinion, only the limiting case for small ψ_∞ is of importance, i.e. the case treated in Paragraph 12.

$$\lim_{\substack{R=\infty \\ \psi_R = \rho/}} \psi_R R = \infty .$$

14. Determination of the Effective Cross Section in Case II (Case of Intersection)

Here we are assuming with Landau [8] that if the intersection is located in the imaginary ν, the transition probabilities $\left|\eta_{1J}\right|^2$ disappear in comparison with the real case. For very small real intersection velocities

$$v_J = \sqrt{p_\infty^2 - \frac{J^2}{r_0^2}} \cong 0,$$

i.e. for $J \cong \rho_m r_0 = J_m$ the Landau $\left|\eta_{1J}\right|^2$ would be $\gg 1/4$. Our method (paragraph 9) is not valid for very small but it is valid while

$$\frac{\alpha^2}{\psi' p_m} < \int_{r_0=0}^{r} \nu_0 \, dr < p_m \cdot (r_0 - r_{\nu_0=0}).$$

However, our $\left|\eta_{1J}\right|^2$ never exceeds $1/4$. It is therefore valid longer than Landau's formula. If the function

$$f_2(k) = \int_0^1 dz \cdot \left(e^{-k\frac{z}{1-z}} - e^{-2k\frac{z}{1-z}} \right)$$

is introduced and

$$z = \frac{J^2}{p_\infty^2 r_0^2} = \frac{J^2}{J_m^2},$$

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then the cross section, due to (7), (10), (17) and (29) becomes

$$q = \pi r_0^2 \cdot 2 \left(\frac{p_m}{p_\infty}\right)^2 \cdot f_2\left(\pi \frac{\Lambda^2 p_m}{r_0^2 \psi'}\right); \quad q \cong 0 \text{ for } p_\infty^2 < 0. \tag{42}$$

The function f_2 is for $k \ll 1$ equal to $4k/3$, attains a broad maximum of the value of 0.164 and for large values of k behaves like $\frac{1}{2}k$. For small k values,

(42) passes into the Landau expression (Landau's equation (27)). The maximum effective cross section in case II is thus of the order of magnitude of πr_0^2, where r_0 is the radius of the intersection location.

Let us plot a "resonance curve" in order to compare size conditions in case I and II and let us set

$$r_0 = 10^{-8}\,\text{cm},\quad M = 10\,M_H.$$

Let us set $\psi_\infty \cdot 10^8$ for ψ', because ψ_∞ is frequently attained at r = 2 to 3 atomic diameters (10^{-8} cm). The value of q from Equation (42) can then be compared with the q. This comparison is performed in Figure 6.

It is seen immediately that the case of intersection (42) does not possess the character of a "resonance process", because for increasing resonance sharpness the effective cross section declines only as does $1/\psi$. Experimental results however (a compilation is found in Kallmann and London [5], with more recent measurements by Zemansky [14]) show a distinct resonance character.

Concerning the order of magnitude, Figure 8 shows that - in contrast to Landau's opinion - effective cross sections in the vicinity of resonance without intersection are mainly larger than those with intersection. They exceed even gas kinetic cross sections.[17]

15. The Ionization of Inert Gases by Alkali Ions

The case of intersection has another meaning also. Weizel and Beeck [4] explained the results of Beeck and Mouzon [3] by the intersection of potential curves. The experimental results are briefly the following:

The ionization of an inert gas by the collision of positive ions increases at an ion velocity with a kinetic energy substantially higher than the ionization energy, abruptly. /420 Under this kinetic velocity, the ionization observed is of a smaller order of magnitude. Ordinary ionization by the impact of heavy particles can, at least qualitatively, represented by the method of Morse and Stueckelberg [6] (paragraph 4, Equation (36) and Figure 3). (In this figure, $\beta = 10$ must be chosen). No sudden onset can occur there. A collision

17. The effective cross section and the resonance character can be brought close to case I in case II by letting r_0 grow with decreasing ψ_∞.

of the first kind must be involved, because the presence of slow electrons is observed.

Weizel and Beeck explain the process by the intersection of the potential curves of K+ + A and K+ + A+. They do not mention, however, the fact that this involves the intersection of the potential curve $K^+ + A$ with the family of curves $K^+ + A^+$, corresponding to the different real velocities v of the separate electrons in the infinite. However, each of these infinitely close curves has another intersection and another matrix element.

It appears hopeless to execute this problem in the complex range. For the approximation method in (42) ($f_2(k) = 4/3\ k$), however, if dQ_v/dv is the number of electron states per dv:

$$q = \int dq_v = \frac{8\pi^2}{3} \cdot \int_0^\infty \frac{p_m^3}{p_0^2} \cdot \frac{\Lambda_v^2}{\psi_r'} \cdot \frac{dQ_v}{dv} \cdot dv.$$

It is known that $\Lambda_v^2\ dQ/dv$ rapidly decreases with rising (see Morse and Stueckelberg [3], p. 597) and that it has its maximum value at $v = 0$ [15]. We therefore replace the integral $\Lambda_v^2 \cdot (dQ/dv)dv$ by the average value of Λ^2. This means that the infinite number of potential curves is replaced by an average curve which is very near the curve for $v = 0$.

Without discussing whether the curves intersect (see (14)), let us assume that intersection takes place. Then, if V_0 and r_{0A}, measured in volt and A, are the coordinates of the intersection[18] and if ψ_V', measured in volt per A, and V the volt velocity of the positive ions, in place of (42): /421

$$q = 3{,}78 \times 10^{-17} \cdot \frac{\Lambda^2}{\psi_r' \cdot \sqrt{m}} \cdot \frac{(V - V_0)^{\frac{3}{2}}}{V} \cdot \frac{3}{4k} \cdot f_2(k)$$

$$k = 4{,}48 \times 10^{-2} \cdot \frac{\Lambda^2}{\psi_r' \cdot \sqrt{m}} \cdot \frac{1}{r_{0A}^2} \cdot (V - V_0)^{\frac{1}{2}}$$

$$m = M/10\,M_H. \qquad (43)$$

Nordmeyer [3] performed newer measurements of $K^+ + A \rightarrow K^+ + A^+$, which essentially confirm the results of Beeck and Mouzon [3], but extend them to higher velocities (to 1000 volt). His measured points are compared in Figure 9 logarithmically with Equation (43). A value was selected for V_0 so that the first points are located on a straight line below 45° (small $k: 3f_2(k)/4k = 1$). Since $M \cong 40 \times 40/80 = 20$ m = 2. /422

18. In the diagram of the potential energy curves (Figure 1)/V_0 then $E(r_0)-E(\infty)$ on Curve A_0, measured in volt.

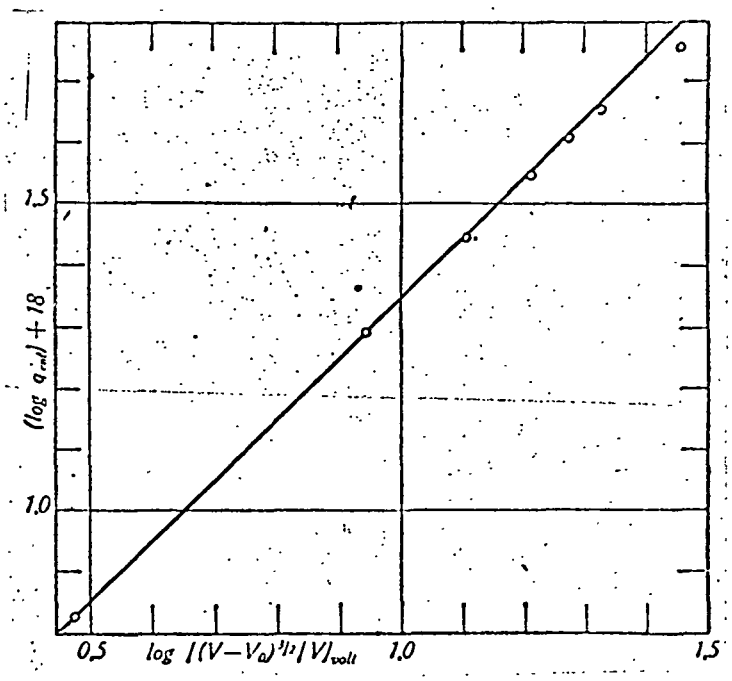

Figure 9. Effective cross section q for the ionization of argon by potassium ions as a function of $(V-V_0)^{3/2}$ in cm^2 and $\sqrt{Volt}$ on a Log Scale. (ψ_V'/Λ^2 = 23.8 Volt/cm^2). The straight line is below 45°. The points plotted represent points measured by Nordmeyer.

From this:

$$V_0 = 55 \text{ Volt}; \quad \frac{\Lambda^2}{\psi_V'} = 0{,}42 \text{ Å Volt}^{-1}.$$

The higher measured points yield the deviation of $3f_2/4k$ from 1. For 1000 volt, this deviation corresponds to a k value of the order of 0.02. If ψ_V' = 16 V/1 Å, then Λ^2 is 0.67. The order of magnitude determination of k yields r_0 at 1.5 Å.

The explanation by Weizel-Beeck thus appears to be correct even quantitavely. It would be of interest to extend the experiments to higher velocities in order to determine the maximum at k = 1. If the estimate of r_0 is correct, the maximum is at approximately 500,000 volt, but its value is only about twice that at 1000 volt.

16. Summary

A link method of approximation functions of two conjugated differential equations i corresponding to the W.K.B [2] process, has been developed.

The method may be applied to collisions of the second kind between atoms. Two cases are distinguished. In case I (paragraph 10) the potential energy curves responsible for elastic motion do not intersect in zero order approximation. In case II (paragraph 9), they intersect at real velocities. In certain cases the link method may be replaced by the conventional perturbation method. (paragraphs 6 and 11).

Application to the determination of effective cross sections for collisions of the second kind shows that essentially case I is responsible for the

phenomenon (paragraph 14). For collisions between positive ions and atoms, on the other hand, case II should be of importance (15).

Another potential application of the method described is predissociation and possibly the processes taking place during the collision of particles and atomic nuclei.

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